

# **Aerobic Oxidation in Nanomicelles of Terminal Alkynes, in Water at Room Temperature\*\***

Sachin Handa, James C. Fennewald, Shane Rainey, and Bruce H. Lipshutz\*

Department of Chemistry & Biochemistry

University of California, Santa Barbara, CA 93106

PHONE: 805-893-2521

FAX: 805-893-8265

\*lipshutz@chem.ucsb.edu

<http://www.chem.ucsb.edu/~lipshutzgroup/>

## **Supporting Information**

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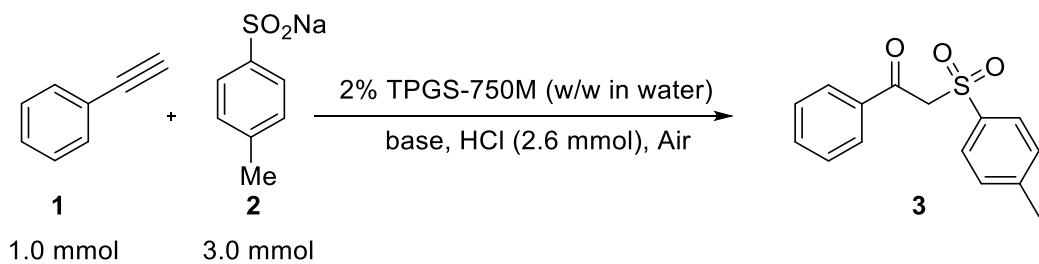


## 1. General Experimental Details

All manipulations were carried out under air unless otherwise noted. TLC plates (UV 254 indicator, glass backed, thickness 200 mm) and silica gel (standard grade, 230 – 400 mesh) were purchased from Merck. Diethyl ether, THF, ethyl acetate, and hexanes was purchased from Fisher Scientific. THF was taken from Innovative Technologies Solvent Purification System (SPS) and used immediately. NiPr<sub>2</sub>Et, NEt<sub>3</sub>, morpholine, pyridine, 2,6-lutidine, and 2,4,6-collidine were distilled and stored on activated 4 Å molecular under argon. NMR solvents were purchased from Cambridge Isotopes Laboratories. All nanomicellar aerobic oxidation reactions were either performed in 4 mL reaction vials on a reaction block for circular top hot plate stirrer at RT or 10 mL round-bottomed flasks. All Sonogashira coupling reactions were performed in dry glassware under the atmosphere of argon. Reaction vials (4 mL with green top polypropylene cap and PTFE septa) were purchased from Chemglass Life Sciences, and used without further drying. Reaction vials were also recycled and re-used. HPLC grade water was used to prepare surfactant solution. TPGS-750M was synthesized by a published procedure,<sup>1</sup> and is also commercially available from Sigma-Aldrich. Melting points were determined using a MEL-TEMP II melting point apparatus with samples in Kimble Kimex 51 capillaries (1.5-1.8 x 90 mm). NMR spectra were recorded at 23 °C on Varian Unity INOVA (400, 500 and 600 MHz) spectrometers. Reported chemical shifts are referenced to residual solvent peaks.<sup>2</sup>. IR spectra were acquired on a FTIR Perkin Elmer Spectrum Two: UATR Two spectrometer using 1 cm<sup>-1</sup> resolution. High resolution mass analyses were obtained using a 5975C Mass Selective Detector, coupled with a 7890A Gas Chromatograph (Agilent Technologies) as capillary column a HP-5MS cross-linked 5% phenylmethyl- polysiloxanediphenyl column (30 m x 0.250 mm, 0.25 micron, Agilent Technologies) was employed. Helium was used as carrier gas at a constant flow of 1 mL/min.

## 2. Optimizations of Nanomicellar Aerobic Oxidation

**Note:** Effective stirring, neutralization of aryl sodium sulfinate, and grinding of reactants in to a powder form are important determinants of the reaction. All reactions were performed in the presence of light, reactions in the dark were found to be difficult to initiate.



## **2a. Finding a base to enhance the lifetime of arylsulfinic acids<sup>a</sup>**

Entry	Base (2.5 mmol)	Time (h)	% yield <b>3<sup>b</sup></b>
1	Triethylamine	6	78
2	Pyridine	8	56
3	<i>N,N</i> -Diisopropylethylamine	16	70
4	<b>2,6-Luitidine</b>	8	<b>80</b>
5	DMAP	4	78 <sup>c</sup>
6	Morpholine	12	66
7	— <sup>c</sup>	24	No reaction

<sup>a</sup> Reaction conditions: 0.5 M phenylacetylene in 2% TPGS-750M, RT, air balloon, except phenylacetylene solution, other reagents were added in two portions in 80 minutes interval.

<sup>b</sup>Crude NMR yield; <sup>c</sup> Sodium sulfinate was not neutralized by HCl, and no base was added.

**2b. Equivalents of 2,6-lutidine required with respect to 3.0 equivalents of sodium *p*-tolylsulfinate**

Entry	2,6-lutidine (mmol)	Time (h)	%yield <b>3</b>
1	4.0	14	29
2	3.5	14	35
3	3.0	8	70
<b>4</b>	<b>2.5</b>	<b>8</b>	<b>80</b>
5	2.0	7	59

Reaction conditions: 1 mmol, 0.5 M phenylacetylene in 2% TPGS-750M, 3.0 mmol sodium *p*-tolylsulfinate, HCl(3.0 mmol), 2,6-lutidine, RT, air balloon.

Except phenylacetylene solution, other reagents were added in two portions in 80 minutes intervals.

**2c. Optimum amount of sulfinic acid required**

entry	Sodium <i>p</i> -tolylsulfinate (mmol)*	time (h)	% yield <b>3</b>
1	1.0	7	15
2	2.0	7	28
3	3.0	7	80
<b>4</b>	<b>4.0</b>	<b>7</b>	<b>82</b>
5	6.0	7	82
6	10	5	70

\*Sodium *p*-toluenesulfinate was neutralized with 1.0 equivalent of HCl

Reaction conditions: 1 mmol, 0.5 M phenylacetylene in 2% TPGS-750M, RT, air balloon.

Except phenylacetylene solution, other reagents were added in two portions in 80 minutes interval, 2,6-lutidine was used ~10% lesser than the number of equivalents of sulfinic acid. Isolated yields are listed.

## 2d. Effect of concentration on reaction rate

Entry	Conc. (M) <sup>a</sup>	Time (h)	% yield <b>3</b>
1	1.0	12	28
2	0.8	10	35
3	0.5	7	82
<b>4</b>	<b>0.3</b>	<b>6.5</b>	<b>84</b>
5	0.2	7	51

<sup>a</sup> concentration of phenylacetylene (1.0 mmol) in 2% TPGS-750M. Other reaction conditions are: 4.0 mmol sodium *p*-toluenesulfinate), 4.0 mmol HCl , and 3.5 mmol 2,6-lutidine (all these reagents were added in two portions in 80 min interval), RT, air balloon.

## 2e. Effect of surfactant conc. in water

Entry	% (w/w) of TPGS-750M	Time (h)	% yield <b>3</b>
1	0.5	25	10
2	1.0	25	12
<b>3</b>	<b>2.0</b>	<b>6.5</b>	<b>84</b>
4	3.0	6*	50
5	4.0	6*	30

\*extending a reaction time up to 24 h didn't improve the yields.

Other reaction conditions are: 1 mmol, 0.3 M phenylacetylene in TPGS-750M solution in water, 4.0 mmol sodium *p*-toluenesulfinate), 4.0 mmol HCl , and 3.5 mmol 2,6- lutidine (except phenylacetylene, all reagents were added in two portions in 80 min interval), RT, air balloon.

## 2f. Oxygen source and reaction yield

Entry	Oxygen Source	Time (h)	% yield <b>3</b>
1	Pure oxygen	8	51
2	Air	8	70
3	Open vial	8	38
<b>4</b>	<b>Air on oxygenated TPGS</b>	<b>6</b>	<b>84</b>

1 mmol, 0.3 M phenylacetylene in 2% TPGS-750M, 4.0 mmol sodium *p*-toluenesulfinate, 4.0 mmol HCl , and 3.5 mmol 2,6-lutidine (all these reagents were added in two portions in 80 min interval), RT.

## 2g. Choice of surfactant

Entry	2% (w/w) surfactant solution in oxygenated water	time (h)	% yield <b>3</b>
1	Brij 30	Up to 24	8
2	PTS	24	28
<b>3</b>	<b>TPGS-750M</b>	<b>6</b>	<b>84</b>
4	Pluronic	24	8
5	NOK	24	59
6	PQS	8	traces*

1 mmol, 0.3 M phenylacetylene in 2% surfactant, 4.0 mmol sodium *p*-toluenesulfinate, 4.0 mmol HCl , 3.5 mmol 2,6-lutidine (all these reagents were added in two portions in 80 min interval), RT, air balloon;  
\*by TLC.

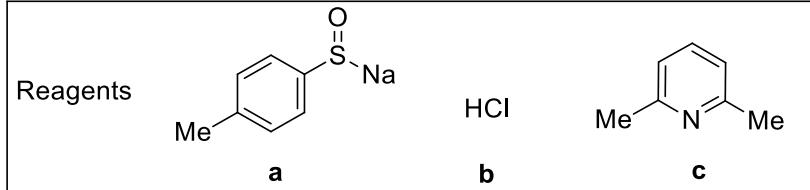
## 2h. Effect of temperature on reaction rate

Entry	Temperature(°C)	Time (h)	% yield 3
1	RT (22)	6	84
2	35	6	80
3	40	5	75
4	45	5	72
5	50	3	60
6	60*	up to 24	<5

\*micellar emulsion found to be broken for this particular reaction at 60 °C

Other reaction conditions: 1 mmol, 0.3M phenylacetylene in 2% surfactant, 4.0 mmol sodium *p*-toluenesulfinate), 4.0 mmol HCl , 3.5 mmol 2,6-lutidine (all these reagents were added in two portions in 80 min interval), air balloon.

## 2i. Effect of a portion-wise addition of reagents on yield



Conditions: Mixing, and then stirring **a** and **b** in TPGS-750M for 3-4 minutes followed by addition of **c**

Entry	<b>a</b> (mmol.)	<b>b</b> (mmol.)	<b>c</b> (mmol.)	% yield <b>14</b>
1	4.0	4.0	3.5	40
*2	2.0	2.0	1.75	84
#3	1.0	1.0	0.9	70

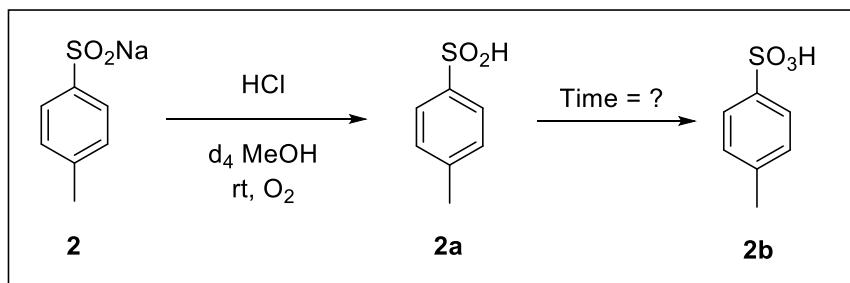
\*after 80 minutes of first addition, same amounts of reagents were sequentially added.

# **a**, **b**, and **c** were added four times after each 80 minutes intervals.

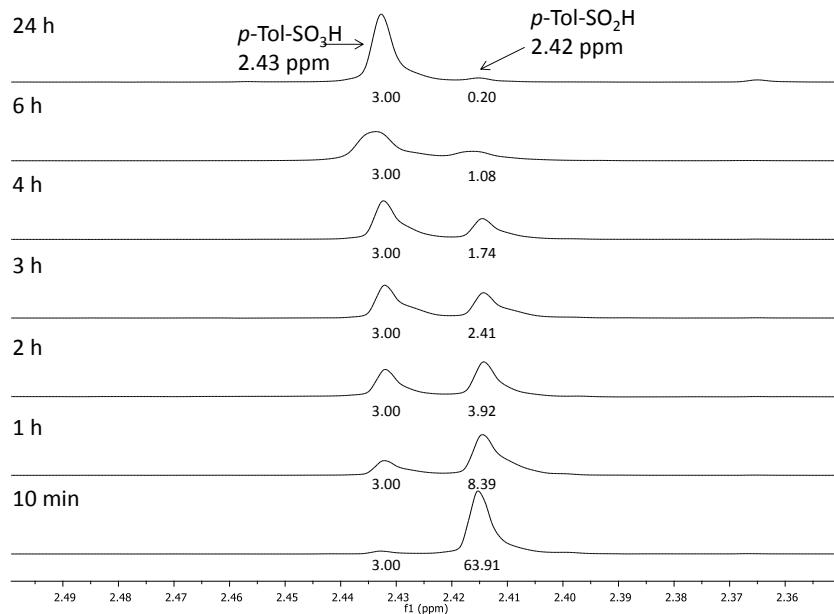
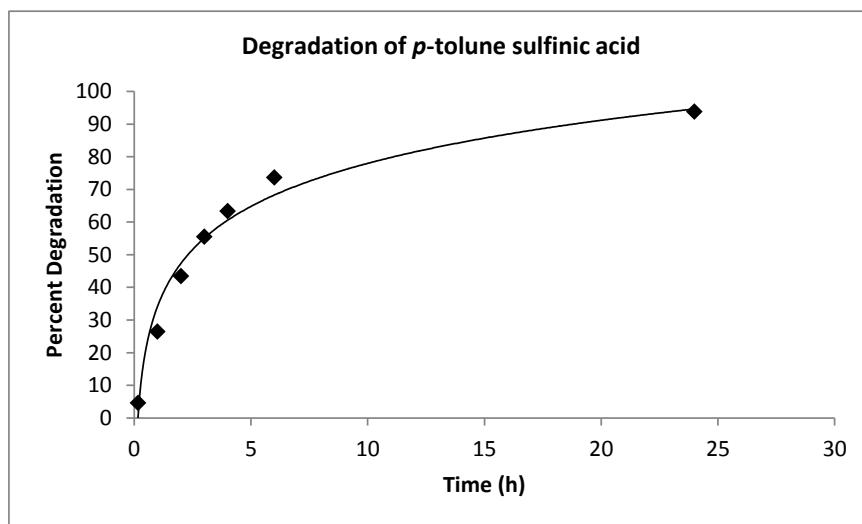
Other reaction conditions: 1 mmol, 0.3M phenylacetylene in 2% surfactant, 4.0 mmol sodium *p*- toluenesulfinate), 4.0 mmol HCl , 3.5 mmol 2,6-lutidine (all these reagents were added in two portions in 80 min interval), RT, air balloon, 6 h.

Portionwise addition of reagents ensures sulfinic acid's availability which otherwise autoxidize as observed in following NMR studies.

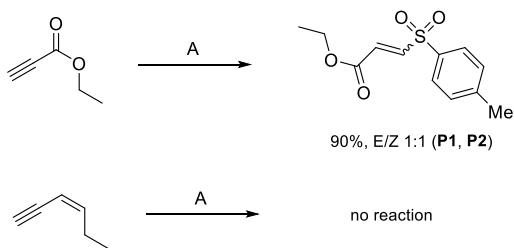
## 2j. Aerobic autoxidation of *p*-toluene sulfinic acid (2)



Conditions: Sulfinic acid (20 mg, 1 equiv.), HCl (9  $\mu$ L, 1 equiv.), d<sub>4</sub>-MeOH, O<sub>2</sub> balloon, rt. Reaction performed in NMR tube.



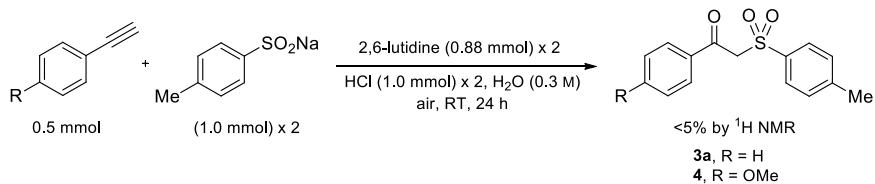
**2k). Conjugation, a key factor for a reaction - Results for substrates offering insufficient stabilization of their vinyl radical intermediates**



Conditions: 1 mmol, 0.3 M **3** or **5** in 2 wt. % TPGS-750-M in oxygenated water, 4.0 mmol sodium *p*-toluenesulfinate, 4.0 mmol HCl\*, 3.5 mmol 2,6-lutidine (all these reagents were added in two portions after 80 min intervals), RT, 7 h, air balloon. \*After HCl addition to the solution of sodium *p*-toluenesulfinate in TPGS-750M, the mixture was stirred for 2-3 min. before addition of 2,6-lutidine.

**2l) Reaction on water**

The corresponding reactions were also run on two educts in neat water in the absence of surfactant under otherwise identical conditions (i.e., “on water”; Scheme 3). Interestingly, <5% of the anticipated product in each case was seen (by  $^1\text{H}$  NMR), with the majority of the mass associated with unidentified side products and starting materials, clearly indicative of the importance of TPGS-750-M in the aqueous medium.



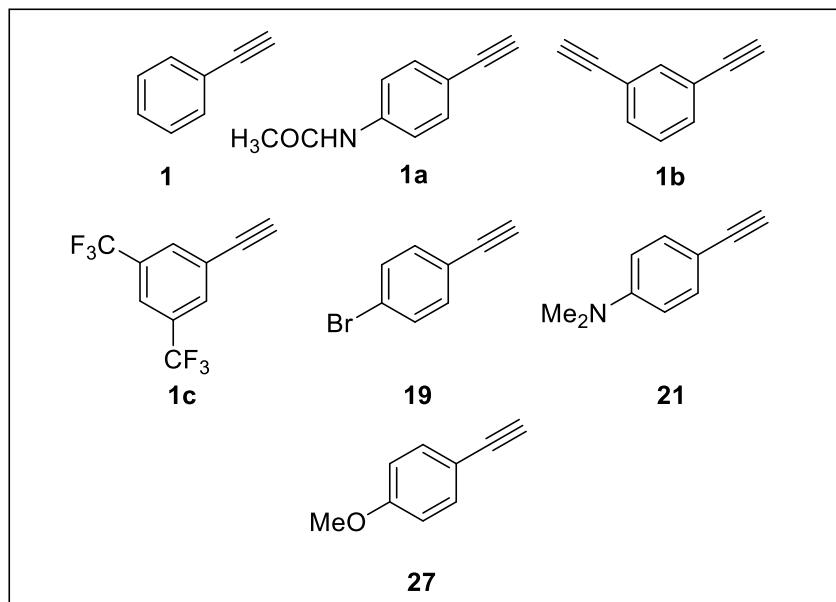
**3. General Procedure For Synthesis Of Substrates**

**A) Synthesis of alkynes:** All alkynes were synthesized following a modified general procedure. Under inert atmosphere, aryl bromide or iodide (1.0 equivalent) was placed in an oven-dried two-neck round bottomed flask fitted with reflux condenser containing dry THF (2 mL/mmol of arylacetylene) at RT. Triethylamine (10.0 equivalents) was added by syringe followed by addition of trimethylsilylacetylene (1.5 equivalents),  $\text{Pd}(\text{PPh}_3)_4$  (0.5 mol%), and  $\text{CuI}$  (0.01

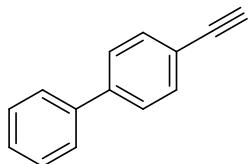
mol%). The reaction mixture was stirred for 6-8 h at 60 °C under atmosphere of argon. The reaction mixture was cooled to RT, and filtered through a Celite pad using additional minimum amount of hexanes. The organic layer was collected and washed sequentially with 0.5 M cold HCl, water, and brine. The volatiles were removed under reduced pressure to obtain crude product as viscous brown oil. The crude product was dissolved in a minimum amount of THF, and the reaction mixture was cooled to 0 °C. Tetrabutylammonium fluoride (1.5 equiv, 1.0 M solution in THF) was added and reaction mixture was stirred for 30 min at RT. The reaction mixture was diluted with a minimum amount of hexanes and sequentially washed with water, sodium bicarbonate, and brine to obtain a crude product as brown oil. The crude material was purified by flash chromatography using silica gel eluting with ether/hexanes (1:99).

#### 4. Analytical data for substrates

Arylacetylenes **1**, **1a**, **1b**, **1c**, **19**, **21**, and **27** were purchased from commercial sources.

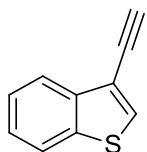


#### 4-Ethynyl-1,1'-biphenyl (**1d**)<sup>3</sup>



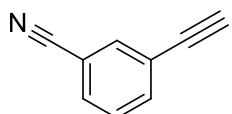
Crystalline white solid, yield 750 mg (95%),  $R_f$  0.51 (1:9 Et<sub>2</sub>O/hexanes). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.59 (d,  $J$  = 7.2 Hz, 2H), 7.56 (s, 4H), 7.45 (t,  $J$  = 7.8 Hz, 2H), 7.37 (t,  $J$  = 7.2 Hz, 1H), and 3.13 (s, 1H).

### **3-Ethynylbenzothiophene (1e)**



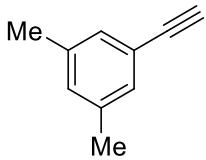
Yellow oil, yield 1.2 g (89%),  $R_f$  0.45 (1:99 Et<sub>2</sub>O/hexanes). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.98 d,  $J$  = 8.0 Hz, 1H), 7.86 (d,  $J$  = 8.0 Hz, 1H), 7.70 (s, 1H), 7.46 (dt,  $J$  = 8.0, 1.5 Hz, 1H), 7.41 (dt,  $J$  = 8.0, 1.0 Hz, 1H), and 3.30 (s, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 139.3, 138.9, 131.5, 125.3, 124.9, 123.1, 122.7, 117.4, 79.9, and 77.5.

### **3-Ethynylbenzonitrile (1f)<sup>4</sup>**



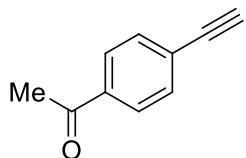
Crystalline white solid, yield 890 mg (91%),  $R_f$  0.39 (1:40 Et<sub>2</sub>O/hexanes). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (s, 1H), 7.70 (d,  $J$  = 7.6 Hz, 1H), 7.63 (d,  $J$  = 7.6 Hz, 1H), 7.45 (t,  $J$  = 8.0 Hz, 1H), and 3.19 (s, 1H).

### **1-Ethynyl-3,5-dimethylbenzene (1g)<sup>5</sup>**



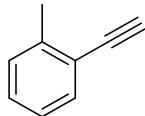
Yellow oil, yield 2.0 g (92%),  $R_f$  0.72 (1:99 Et<sub>2</sub>O/hexanes). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.13 (s, 2H), 6.99 (s, 1H), 3.01 (s, 1H), and 2.30 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  138.0, 130.8, 129.9, 121.8, 84.1, 76.5, and 21.2.

### **1-(4-Ethynylphenyl)ethanone (1h)<sup>6</sup>**



Crystalline white solid, yield 1.3 g (92%),  $R_f$  0.55 (1:99 Et<sub>2</sub>O/hexanes). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.91 (d,  $J$  = 7.2 Hz, 2H), 7.57 (d,  $J$  = 7.2 Hz, 2H), 3.25 (s, 1H), and 2.60 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  197.2, 136.8, 132.3, 128.2, 126.9, 82.7, 80.3, and 26.6.

### **2-Ethynyltoluene (ik)**



Clear oil, yield 1.96 g (98%),  $R_f$  0.50 (hexanes). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.47 (d,  $J$  = 7.6 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.17 – 7.12 (m, 1H), 3.28 (s, 1H), 2.47 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  40.8, 132.5, 129.4, 128.7, 125.5, 121.9, 103.7, 82.5, 80.9, and 20.6.

## **5. General procedure for nanomicellar aerobic oxidations**

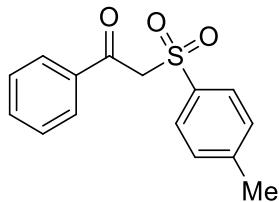
**Note:** All reactions were run on either 1.0 mmol or 0.5 mmol scales of arylacetylene. Effective stirring was an important parameter in all reactions.

In a 4.0 mL reaction vial, 1 mmol of arylacetylene was dissolved in 3.3 ml of 2% TPGS-750 M in water, and the mixture was stirred for 3 min at RT (homogenous emulsion was formed within 3 min). In a 10 mL round-bottomed flask equipped with Teflon coated magnetic stir bar, 2.0 mmol sodium arylsulfinate was dissolved in a minimum amount of 2 wt. % TPGS-750-M in water. HCl (2.0 mmol) was added to the reaction mixture, and mixture was stirred for 2 min at RT under an open air atmosphere, followed by addition of 2,6-lutidine (1.75 mmol). The emulsion of arylacetylene in TPGS-750-M was transferred into a reaction flask containing a mixture of arylsulfinic acid and 2,6-lutidine. The reaction mixture was placed under an atmosphere of air (balloon) and stirred for 80 min at RT. After 80 min, 2.0 mmol sodium arylsulfinate, 2.0 mmol HCl, and 1.75 mmol 2,6-lutidine were sequentially added to the reaction mixture, and mixture was stirred at RT until complete consumption of arylacetylene.

After complete consumption of the starting arylacetylene as monitored by TLC, a minimum amount of warm EtOAc (usually 0.75 mL x 2) was added to the reaction mixture, and mixture was stirred for 3-4 min. After the separation of the organic and aqueous layers, the organic layer was decanted with a pipette, and passed through a silica gel plug already wetted with hexanes. The volatiles were removed under reduced pressure to obtain crude product that was further purified either by crystallization in ether/hexanes or column chromatography using acetone/hexanes as an eluent. Usually, oily compounds were purified by column chromatography over silica gel while solid crude materials were crystallized.

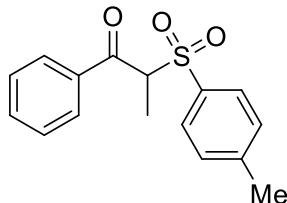
## 6. Analytical data of products

### 1-Phenyl-2-tosylethanone (3a)<sup>7</sup>



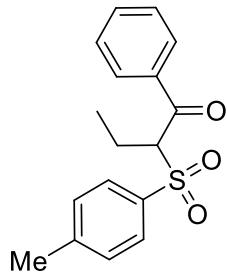
Solid, yield (82%),  $R_f$  0.47 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (d,  $J = 8.4$  Hz, 2H), 7.77 (d,  $J = 8.4$  Hz, 2H), 7.63 (t,  $J = 7.2$  Hz, 1H), 7.49 (t,  $J = 8.4$  Hz, 2H), 7.34 (d,  $J = 8.4$  Hz, 2H), 4.72 (s, 2H), and 2.45 (s, 3H).

### 1-phenyl-2-tosylpropan-1-one (3b)<sup>8</sup>



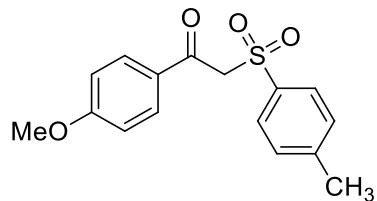
White waxy solid, yield 79 mg (78%),  $R_f$  0.42 (2:3 Et<sub>2</sub>O/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.97 (d,  $J = 7.2$  Hz, 2H), 7.65 (d,  $J = 8.3$  Hz, 2H), 7.60 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.8$  Hz, 2H), 7.30 (d,  $J = 8.0$  Hz, 2H), 5.15 (q,  $J = 6.9$  Hz, 1H), 2.43 (s, 3H), and 1.55 (d,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.7, 145.5, 136.4, 134.1, 133.1, 130.0, 129.6, 129.3, 128.9, 65.1, 21.8, and 13.3.

### 1-phenyl-2-tosylbutan-1-one (3c)<sup>9</sup>



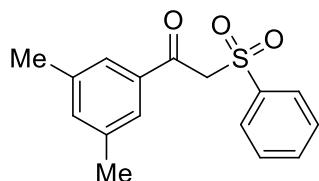
White waxy solid, yield 72 mg (69%),  $R_f$  0.43 (2:3 Et<sub>2</sub>O/hexanes). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.97 (d,  $J$  = 7.2 Hz, 2H), 7.65 (d,  $J$  = 8.3 Hz, 2H), 7.60 (t,  $J$  = 10.5 Hz, 1H), 7.48 (dt,  $J$  = 8.1, 7.5 Hz, 2H), 7.30 (d,  $J$  = 7.9 Hz, 2H), 4.99 (dd,  $J$  = 10.9, 3.6 Hz, 1H), 2.43 (s, 3H), 2.21-1.98 (m, 2H), and 0.88 (t,  $J$  = 7.4 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 192.9, 145.4, 137.6, 134.1, 131.8, 130.0, 129.6, 129.1, 128.9, 71.6, 22.2, 21.8, and 11.6.

### **1-(4-Methoxyphenyl)-2-tosylethanone (4)<sup>10</sup>**



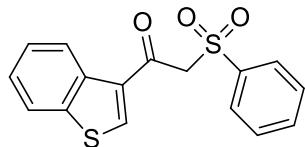
White solid, yield 134 mg (71%), mp 124.5-126.0 °C,  $R_f$  0.41 (2:3 EtOAc/hexanes). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.94 (d,  $J$  = 9.0 Hz, 2H), 7.75 (d,  $J$  = 8.5 Hz, 2H), 7.33 (d,  $J$  = 8.5 Hz, 2H), 6.95 (d,  $J$  = 9.0 Hz, 2H), 4.86 (s, 2H), 3.89 (s, 3H), and 2.44 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 186.5, 164.7, 145.4, 135.9, 132.1, 129.9, 129.1, 128.7, 114.2, 63.8, 55.8, and 21.9.

### **1-(3,5-Dimethylphenyl)-2-(phenylsulfonyl)ethanone (5)**



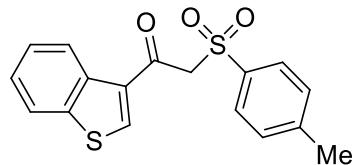
Light yellow solid, yield 224 mg (78%), mp 71-72 °C,  $R_f$  0.41 (4:5 EtOAc/hexanes).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89 (d,  $J = 8.4$  Hz, 2H), 7.66 (t,  $J = 7.2$  Hz, 1H), 7.55 (t,  $J = 7.8$  Hz, 2H), 7.51 (s, 2H), 7.24 (s, 1H), 4.71 (s, 2H), and 2.36 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.3, 138.9, 138.7, 136.2, 135.9, 134.2, 129.3, 128.7, 127.1, 63.5, and 21.3. IR ( $\text{cm}^{-1}$ ) C=O 1645, S=O 1321, 1153; HRMS (ESI,  $[\text{C}_{16}\text{H}_{16}\text{O}_3\text{S} + \text{Na}]^+$ ) calcd 311.0712, found m/z 311.0708.

### **1-(Benzothiophen-3-yl)-2-(phenylsulfonyl)ethanone (6a)**



Solid, yield 122 mg (77%), mp 176-178 °C,  $R_f$  0.34 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.60 (d,  $J = 7.2$  Hz, 1H), 8.52 (s, 1H), 7.90-7.87 (m, 3H), 7.67 (t,  $J = 7.2$  Hz, 1H), 7.54 (t,  $J = 7.6$  Hz, 2H), 7.51-7.43 (m, 2H), and 4.71 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  181.9, 141.7, 139.7, 138.6, 136.3, 134.4, 129.4, 128.7, 126.4, 126.1, 125.5, 122.4, and 66.1. IR ( $\text{cm}^{-1}$ ) C=O 1660, S=O 1314, 1145. HRMS (ESI,  $[\text{C}_{16}\text{H}_{12}\text{O}_3\text{S} + \text{Na}]^+$ ) calcd 339.0126, found m/z 339.0133.

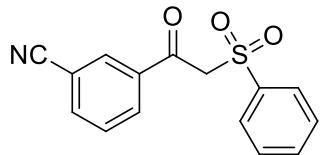
### **1-(Benzothiophen-3-yl)-2-tosylethanone (6b)**



Solid, yield 128 mg (78%), mp 176-177 °C;  $R_f$  0.35 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.60 (d,  $J = 8.5$  Hz, 1H), 8.52 (s, 1H), 7.87 (d,  $J = 7.5$  Hz, 1H), 7.75 (d,  $J = 8.5$  Hz, 2H), 7.50-7.43 (m, 2H), 7.32 (d,  $J = 8.0$  Hz, 2H), 4.69 (s, 2H), and 2.44 (s, 3H).  $^{13}\text{C}$  NMR (126

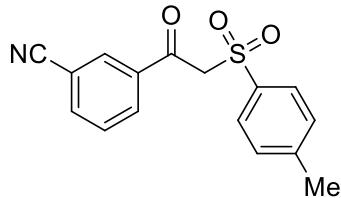
MHz, CDCl<sub>3</sub>): δ 182.1, 145.6, 141.7, 139.8, 136.4, 135.6, 134.5, 130.1, 128.7, 126.4, 126.1, 125.6, 122.5, 66.3, and 21.9. IR (cm<sup>-1</sup>) C=O 1661, S=O 1314, 1145. HRMS (ESI, [C<sub>17</sub>H<sub>14</sub>O<sub>3</sub>S + Na]<sup>+</sup>) calcd 353.0277, found m/z 353.0293.

### **3-(2-(Phenethylsulfonyl)acetyl)benzonitrile (7)**



Sticky solid, yield 99 mg (70%), R<sub>f</sub> 0.34 (2:3 EtOAc/hexanes). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.21 (dd, *J* = 7.0, 1.0 Hz, 1H), 8.19 (s, 1H), 7.89-7.86 (m, 3H), 7.70 (t, *J* = 6.5 Hz, 1H), 7.65 (t, *J* = 6.5 Hz, 1H), 7.57 (t, *J* = 6.5 Hz, 2H), and 4.72 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 186.4, 138.5, 137.2, 136.6, 134.8, 133.4, 133.0, 130.1, 129.6, 128.7, 117.6, 113.8, 63.8, and 29.9. IR (cm<sup>-1</sup>) CN 2885, C=O 1688, S=O 1317, 1146. HRMS (ESI, [C<sub>15</sub>H<sub>11</sub>NO<sub>3</sub>S + Na]<sup>+</sup>) calcd 308.0357, found m/z 308.0366.

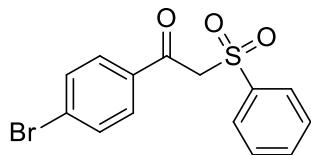
### **3-(2-Tosylacetyl)benzonitrile (8)**



Light yellow solid, yield 106 mg (71%), mp 100-101 °C, R<sub>f</sub> 0.35 (2:3 EtOAc/hexanes). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.22 (d, *J* = 8.0 Hz, 1H), 8.17 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.71 (s, 2H), and 2.46 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 186.6, 146.0, 137.0, 133.0, 130.2, 130.0, 128.6, 117.6, 113.6,

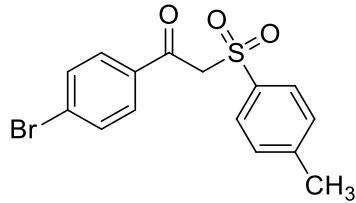
63.9, and 21.9. IR ( $\text{cm}^{-1}$ ) CN 2892, C=O 1683, S=O 1314, 1145; HRMS (ESI,  $[\text{C}_{16}\text{H}_{17}\text{NO}_2\text{S} + \text{Na}]^+$ ) calcd 322..0508, found m/z 322.0513.

**1-(4-Bromophenyl)-2-(phenylsulfonyl)ethanone (9)<sup>11</sup>**



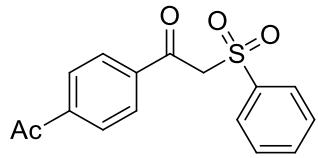
Light yellow solid, yield 128 mg (76%),  $R_f$  0.54 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J = 8.0$  Hz, 2H), 7.82 (d,  $J = 8.5$  Hz, 2H), 7.68 (t,  $J = 7.5$  Hz, 1H), 7.63 (d,  $J = 8.5$  Hz, 2H), 7.56 (t,  $J = 7.5$  Hz, 2H), and 4.69 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.2, 138.7, 134.6, 134.5, 132.4, 130.9, 130.2, 129.4, 128.7, and 63.8.

**1-(4-Bromophenyl)-2-tosylethanone (10)<sup>10</sup>**



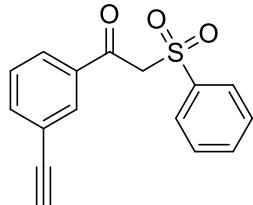
Light yellow solid, yield 144 mg (82%),  $R_f$  0.55 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.82 (d,  $J = 8.5$  Hz, 2H), 7.74 (d,  $J = 8.5$  Hz, 2H), 7.63 (d,  $J = 8.5$  Hz, 2H), 7.34 (d,  $J = 8.5$  Hz, 2H), 4.67 (s, 2H), and 2.45 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.4, 145.7, 134.6, 132.3, 131.0, 130.1, 130.0, 128.7, 63.9, and 21.9.

**1-(4-Acetylphenyl)-2-(phenylsulfonyl)ethanone (11)<sup>12</sup>**



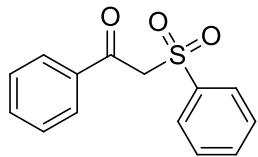
Solid, yield 119 mg (79%),  $R_f$  0.40 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.04 (s, 4H), 7.88 (dd,  $J = 8.5$  Hz, 2H), 7.69 (t,  $J = 7.5$  Hz, 1H), 7.57 (t,  $J = 7.5$  Hz, 2H), 4.76 (s, 2H), and 3.66 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.3, 187.7, 141.1, 138.8, 138.7, 134.6, 129.7, 129.5, 128.7, 128.7, 63.9, and 27.1.

### **1-(3-Ethylphenyl)-2-(phenylsulfonyl)ethanone (12)**



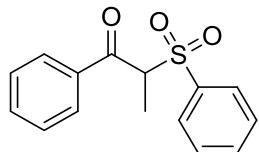
Off-white waxy solid, yield 115 mg (81%),  $R_f$  0.38 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.00 (t,  $J = 2.0$  Hz, 1H), 7.91 (dt,  $J = 8.0, 3.0$  Hz, 1H), 7.89 (dd,  $J = 9.5, 1.5$  Hz, 2H), 7.71-7.65 (m, 2H), 7.56 (dt,  $J = 8.0, 1.5$  Hz, 2H), 7.45 (t,  $J = 7.5$  Hz, 1H), 4.72 (s, 2H), and 3.15 (s, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.4, 138.7, 137.6, 135.9, 134.5, 132.9, 129.5, 129.4, 129.1, 128.7, 123.2, 82.2, 79.1, and 63.6. IR ( $\text{cm}^{-1}$ ) CCH 3271, C=O 1678, S=O 1316, 1133. HRMS (ESI,  $[\text{C}_{16}\text{H}_{12}\text{O}_3\text{S} + \text{Na}]^+$ ) calcd 307.0399, found m/z 307.0404.

### **1-Phenyl-2-(phenylsulfonyl)ethanone (13a)<sup>11</sup>**



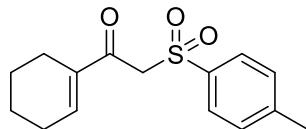
Off-white solid, yield 202 mg (78%),  $R_f$  0.52 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93 (dd,  $J = 8.0, 1.0$  Hz, 2H), 7.90 (dd,  $J = 8.0, 1.0$  Hz, 2H), 7.66 (dt,  $J = 7.5, 1.0$  Hz, 1H), 7.62 (dt,  $J = 7.5, 1.0$  Hz, 1H), 7.56 (t,  $J = 7.5$  Hz, 2H), 7.48 (t,  $J = 7.5$  Hz, 2H), and 4.74 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.1, 138.9, 135.8, 134.5, 134.4, 129.4, 129.3, 129.0, 128.7, and 63.6.

### **1-phenyl-2-(phenylsulfonyl)propan-1-one (13b)<sup>13</sup>**



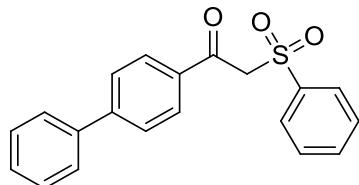
Off-white solid, yield 77 mg (76%),  $R_f$  0.42 (2:3 Et<sub>2</sub>O/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.97 (dd,  $J = 8.4, 1.2$  Hz, 2H), 7.79 (dd,  $J = 8.4, 1.2$  Hz, 2H), 7.72-7.42 (m, 6H), 5.17 (q,  $J = 6.9$ , 1H), and 1.57 (d,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.6, 136.3, 134.3, 134.2, 129.9, 129.3, 129.0, 128.9, 126.2, 65.1, and 13.3.

### **1-(cyclohex-1-en-1-yl)-2-tosylethan-1-one (14)**



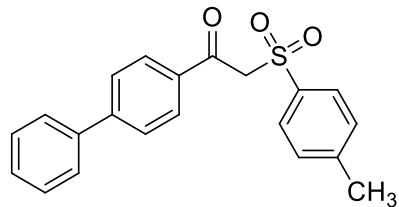
Off-white waxy solid, yield 69 mg (62%),  $R_f$  0.38 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.74 (d,  $J = 8.1$  Hz, 2H), 7.33 (d,  $J = 7.9$  Hz, 2H), 6.98 (s, 1H), 4.40 (s, 2H), 2.43 (s, 3H), 2.28 (s, 2H), 2.16 (s, 2H), and 1.59 (s, 4H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.6, 146.1, 145.3, 139.4, 136.2, 129.9, 128.7, 62.6, 26.7, 23.1, 21.8, 21.7, and 21.3. IR ( $\text{cm}^{-1}$ ) C=O 1667, S=O 1384, 1149; HRMS (ESI,  $[\text{C}_{15}\text{H}_{18}\text{O}_3\text{S} + \text{Na}]^+$ ) calcd 301.0874, found m/z 301.0883.

**1-([1,1'-Biphenyl]-4-yl)-2-(phenylsulfonyl)ethanone (15)<sup>11</sup>**



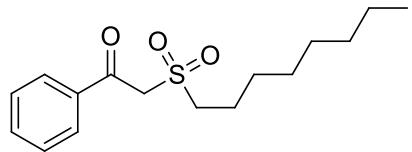
Solid, yield 120 mg (72%),  $R_f$  0.46 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.02 (d,  $J = 8.5$  Hz, 2H), 7.92 (d,  $J = 7.5$  Hz, 2H), 7.70 (d,  $J = 8.5$  Hz, 2H), 7.67 (t,  $J = 8.5$  Hz, 1H), 7.62 (d,  $J = 7.5$  Hz, 2H), 7.56 (t,  $J = 7.5$  Hz, 2H), 7.48 (t,  $J = 7.5$  Hz, 2H), 7.44 (t,  $J = 7.5$  Hz, 1H), and 4.77 (s, 2H).

**1-([1,1'-Biphenyl]-4-yl)-2-tosylethanone (16)**



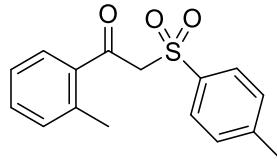
Solid, yield 122 mg (70%), mp 116-117 °C,  $R_f$  0.51 (1:1 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.03 (d,  $J = 8.5$  Hz, 2H), 7.78 (d,  $J = 8.0$  Hz, 2H), 7.70 (d,  $J = 8.5$  Hz, 2H), 7.63 (d,  $J = 7.5$  Hz, 2H), 7.49 (d,  $J = 7.5$  Hz, 1H), 7.48 (d,  $J = 7.5$  Hz, 1H), 7.42 (t,  $J = 7.5$  Hz, 1H), 7.35 (d,  $J = 8.0$  Hz, 2H), 4.74 (s, 2H), and 2.45 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.8, 147.2, 145.5, 139.6, 135.9, 134.6, 130.2, 130.0, 129.2, 128.8, 128.7, 127.6, 127.5, 62.9, and 21.9. IR ( $\text{cm}^{-1}$ ) C=O 1661, S=O 1314, 1145. HRMS (ESI,  $[\text{C}_{17}\text{H}_{14}\text{O}_3\text{S} + \text{Na}]^+$ ) calcd 373.0869, found m/z 373.0873.

**2-(Octylsulfonyl)-1-phenylethanone (17)<sup>11</sup>**



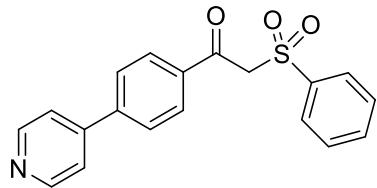
Solid, yield 114 mg (77%),  $R_f$  0.52 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.01-7.99 (m, 2H), 7.65-7.63 (m, 1H), 7.52-7.50 (m, 2H), 4.55 (s, 2H), 3.25 (t,  $J = 6.5$  Hz, 2H), 1.90-1.86 (m, 2H), 1.47-1.43 (m, 2H), 1.33-1.24 (m, 8H), and 0.87 (t,  $J = 6.4$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  189.4, 135.9, 134.8, 129.5, 129.1, 59.7, 53.9, 31.8, 29.1, 29.0, 28.5, 22.7, 22.0, and 14.2.

### **1-(o-tolyl)-2-tosylethan-1-one (18)**



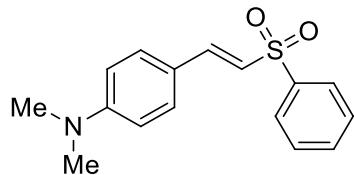
Solid, yield 120 mg (71%), mp 109-111 °C,  $R_f$  0.40 (1:1 Et<sub>2</sub>O/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.74 (t,  $J = 9.2$  Hz, 3H), 7.42 (td,  $J = 7.5, 1.0$  Hz, 1H), 7.33 (d,  $J = 8.1$  Hz, 2H), 7.30 – 7.23 (m, 2H), 4.68 (s, 2H), 2.44 (s, 3H), and 2.43 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.49, 145.23, 140.04, 136.03, 135.74, 132.74, 132.28, 130.41, 129.81, 128.51, 125.90, 103.73, 103.73, 65.62, 21.70, and 21.53. IR ( $\text{cm}^{-1}$ ) C=O 1684, S=O 1309, 1141; HRMS (ESI,  $[\text{C}_{16}\text{H}_{16}\text{O}_3\text{S} + \text{Na}]^+$ ) calcd 311.0718, found m/z 311.0716.

### **2-(phenylsulfonyl)-1-(4-(pyridin-4-yl)phenyl)ethan-1-one (20)**



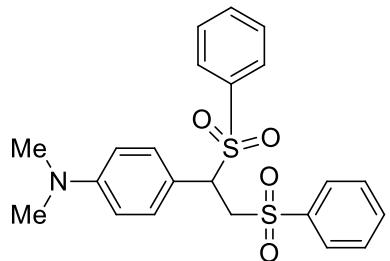
Off-white solid, yield 79 mg (54%), mp 134-136 °C,  $R_f$  0.40 (7:3 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.72 (d,  $J$  = 6.0 Hz, 2H), 8.08 (d,  $J$  = 8.2 Hz, 2H), 7.91 (d,  $J$  = 7.7 Hz, 2H), 7.75 (d,  $J$  = 8.1 Hz, 2H), 7.69 (td,  $J$  = 7.6, 0.8 Hz, 1H), 7.57 (t,  $J$  = 7.7 Hz, 2H), 7.52 (d,  $J$  = 6.1 Hz, 2H), 4.77 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.4, 150.6, 146.6, 143.9, 138.6, 135.8, 134.4, 130.2, 129.3, 128.6, 127.5, 121.7, 103.7, 63.7. IR ( $\text{cm}^{-1}$ ) C=O 1668, S=O 1311, 1145; HRMS (ESI,  $[\text{C}_{19}\text{H}_{15}\text{NO}_3\text{S} + \text{Na}]^+$ ) calcd 360.0665, found m/z 360.0657.

### (E)-N,N-Dimethyl-4-(2-(phenylsulfonyl)vinyl)aniline (22)



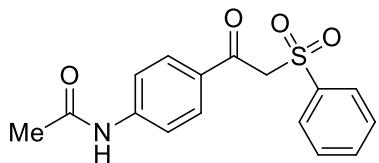
White solid, yield 255 mg (89%), mp 118-119 °C,  $R_f$  0.43 (3:2 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.73 (d,  $J$  = 7.00 Hz, 2H), 7.50 (t,  $J$  = 7.5 Hz, 1H), 7.40 (t,  $J$  = 7.5 Hz, 2H), 7.25 (d,  $J$  = 8.5 Hz, 2H), 6.57 (d,  $J$  = 9.0 Hz, 2H), 6.49 (s, 1H), 5.87 (s, 1H), and 2.94 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.0, 150.9, 139.6, 133.2, 130.1, 128.9, 128.3, 123.8, 111.7, 103.9, and 40.3. IR ( $\text{cm}^{-1}$ ) C=C 1608, S=O 1363, 1141; HRMS (ESI,  $[\text{C}_{16}\text{H}_{17}\text{NO}_2\text{S} + \text{Na}]^+$ ) calcd 310.0878, found m/z 310.0872.

### 4-(1,2-bis(Phenylsulfonyl)ethyl)-N,N-dimethylaniline (23)



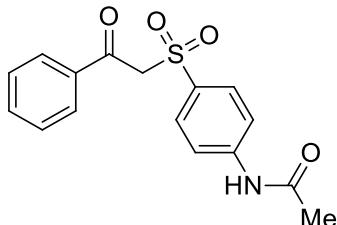
White solid, yield 347 mg (81%), mp 175-176 °C,  $R_f$  0.41 (4:5 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59 (m, 5H), 7.47 (t,  $J$  = 7.5 Hz, 1H), 7.41 (dt,  $J$  = 7.5, 1.5 Hz, 2H), 7.31 (dt,  $J$  = 7.5, 1.5 Hz, 2H), 6.72 (d,  $J$  = 9.0 Hz, 2H), 6.33 (d,  $J$  = 9.0 Hz, 2H), 4.52 (dd,  $J$  = 12.0, 2.5 Hz, 1H), 4.10 (dd,  $J$  = 14.5, 2.5 Hz, 1H), 3.94 (dd,  $J$  = 14.5, 12.0 Hz, 1H), and 2.89 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 151.0, 139.5, 136.5, 134.1, 133.5, 130.1, 129.3, 129.0, 129.0, 128.0, 115.2, 112.0, 66.1, 54.1, and 40.3. IR ( $\text{cm}^{-1}$ ) S=O 1303, 1138; HRMS (ESI,  $[\text{C}_{22}\text{H}_{23}\text{NO}_4\text{S}_2 + \text{H}]^+$ ) calcd 430.1147, found m/z 430.1150.

### **N-(4-(2-(Phenylsulfonyl)acetyl)phenyl)acetamide (25)**



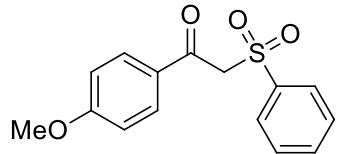
White solid, yield 87 mg (69%), mp 219-220 °C,  $R_f$  0.38 (1:1 acetone/hexanes).  $^1\text{H}$  NMR (500 MHz, D6-DMSO):  $\delta$  10.33 (s, 1H), 7.91-7.89 (m, 4H), 7.73 (t,  $J$  = 7.5 Hz, 1H), 7.67 (d,  $J$  = 9.0 Hz, 2H), 7.63 (t,  $J$  = 7.5 Hz, 2H), 5.23 (s, 2H), and 2.09 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz, D6-DMSO):  $\delta$  187.2, 169.1, 144.5, 139.6, 133.9, 130.6, 130.3, 129.2, 128.0, 118.0, 61.9, and 24.3. IR ( $\text{cm}^{-1}$ ) C=O 1694, 1667, S=O 1283, 1159; HRMS (ESI,  $[\text{C}_{16}\text{H}_{15}\text{NO}_4\text{S} + \text{Na}]^+$ ) calcd 340.0614, found m/z 340.0614.

**N-(4-((2-Oxo-2-phenylethyl)sulfonyl)phenyl)acetamide (26)**



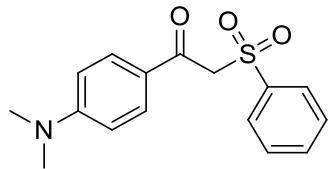
Light yellow solid, yield 114 mg (72%), mp 153-155 °C,  $R_f$  0.38 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.94 (d,  $J$  = 8.5 Hz, 2H), 7.82 (d,  $J$  = 8.5 Hz, 2H), 7.69 (d,  $J$  = 9.0 Hz, 2H), 7.62 (t,  $J$  = 7.5 Hz, 1H), 7.49 (t,  $J$  = 8.0 Hz, 2H), 7.43 (br. s, 1H), 4.72 (s, 2H), and 2.22 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.3, 168.8, 143.5, 135.8, 134.6, 133.2, 130.1, 129.4, 129.0, 119.3, 63.7, and 24.9. IR ( $\text{cm}^{-1}$ ) C=O 1673, 1591, S=O 1315, 1148; HRMS (ESI,  $[\text{C}_{16}\text{H}_{15}\text{NO}_4\text{S} + \text{Na}]^+$ ) calcd 340.0614, found m/z 340.0632.

**1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethanone (28)<sup>11</sup>**



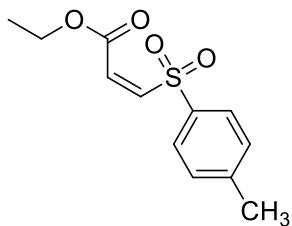
Solid, yield 101 mg (70%),  $R_f$  0.43 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93 (d,  $J$  = 8.5 Hz, 2H), 7.88 (d,  $J$  = 8.5 Hz, 2H), 7.66 (t,  $J$  = 8.0 Hz, 1H), 7.54 (t,  $J$  = 8.0 Hz, 2H), 6.94 (d,  $J$  = 8.5 Hz, 2H), 4.68 (s, 2H), and 3.88 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  186.3, 164.8, 139.1, 134.3, 132.0, 129.3, 129.1, 128.7, 114.3, 63.7, and 55.8.

**1-(4-(Dimethylamino)phenyl)-2-(phenylsulfonyl)ethanone (29)**



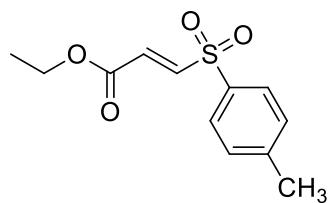
Off-white solid, yield 118 mg (78%), mp 108-109 °C,  $R_f$  0.32 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89 (d,  $J$  = 8.5 Hz, 2H), 7.83 (d,  $J$  = 9.0 Hz, 2H), 7.63 (t,  $J$  = 7.5 Hz, 1H), 7.53 (t,  $J$  = 7.5 Hz, 2H), 6.63 (d,  $J$  = 9.0 Hz, 2H), 4.36 (s, 2H), and 3.08 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 185.0, 154.2, 139.1, 134.1, 132.0, 129.2, 128.7, 123.8, 110.8, 63.4, and 40.1. IR ( $\text{cm}^{-1}$ ) C=O 1660, S=O 1314, 1145; HRMS (ESI,  $[\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S} + \text{Na}]^+$ ) calcd 326.0821, found m/z 326.0842.

#### (Z)-Ethyl-3-tosylacrylate (P1)<sup>14</sup>



Solid, yield 114 mg (45 of 90%),  $R_f$  0.40 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J$  = 8.4 Hz, 2H), 7.36 (d,  $J$  = 7.8 Hz, 2H), 6.49 (AB,  $J$  = 12 Hz, C = 28.2 Hz, 2H), 4.36 (q,  $J$  = 7.2 Hz, 2H), 2.45 (s, 3H), and 1.39 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.2, 145.3, 136.6, 135.5, 131.2, 130.1, 128.4, 62.2, 21.8, and 14.1.

#### (E)-Ethyl-3-tosylacrylate (P2)<sup>15</sup>



Solid, yield 114 mg (90%),  $R_f$  0.40 (2:3 EtOAc/hexanes).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d,  $J = 7.8$  Hz, 2H), 7.38 (d,  $J = 7.8$  Hz, 2H), 7.32 (d,  $J = 15.6$  Hz, 1H), 6.79 (d,  $J = 15.6$  Hz, 1H), 4.24 (q,  $J = 7.2$  Hz, 2H), 2.46 (s, 3H), and 1.30 (t,  $J = 7.2$  Hz, 3H).

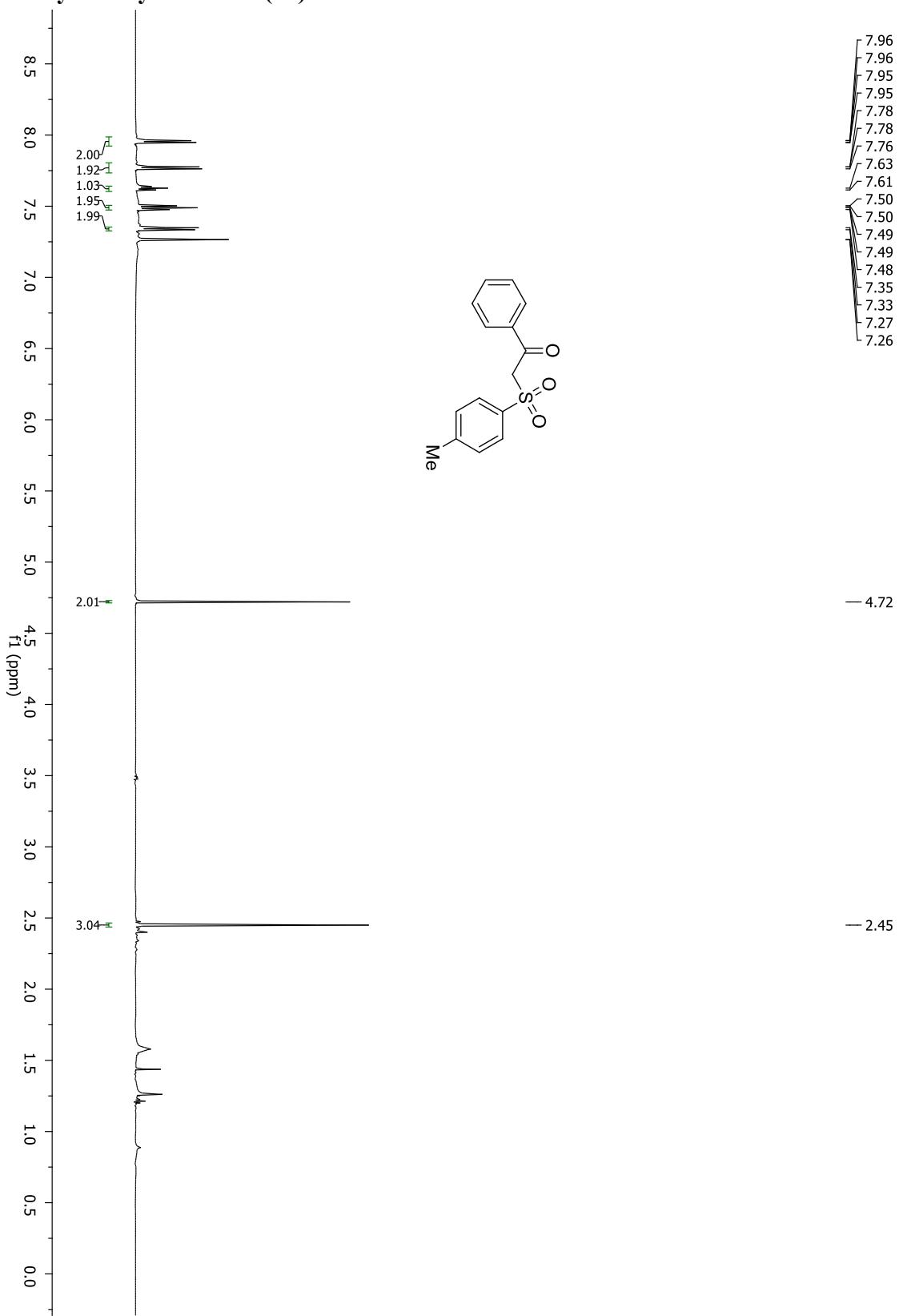
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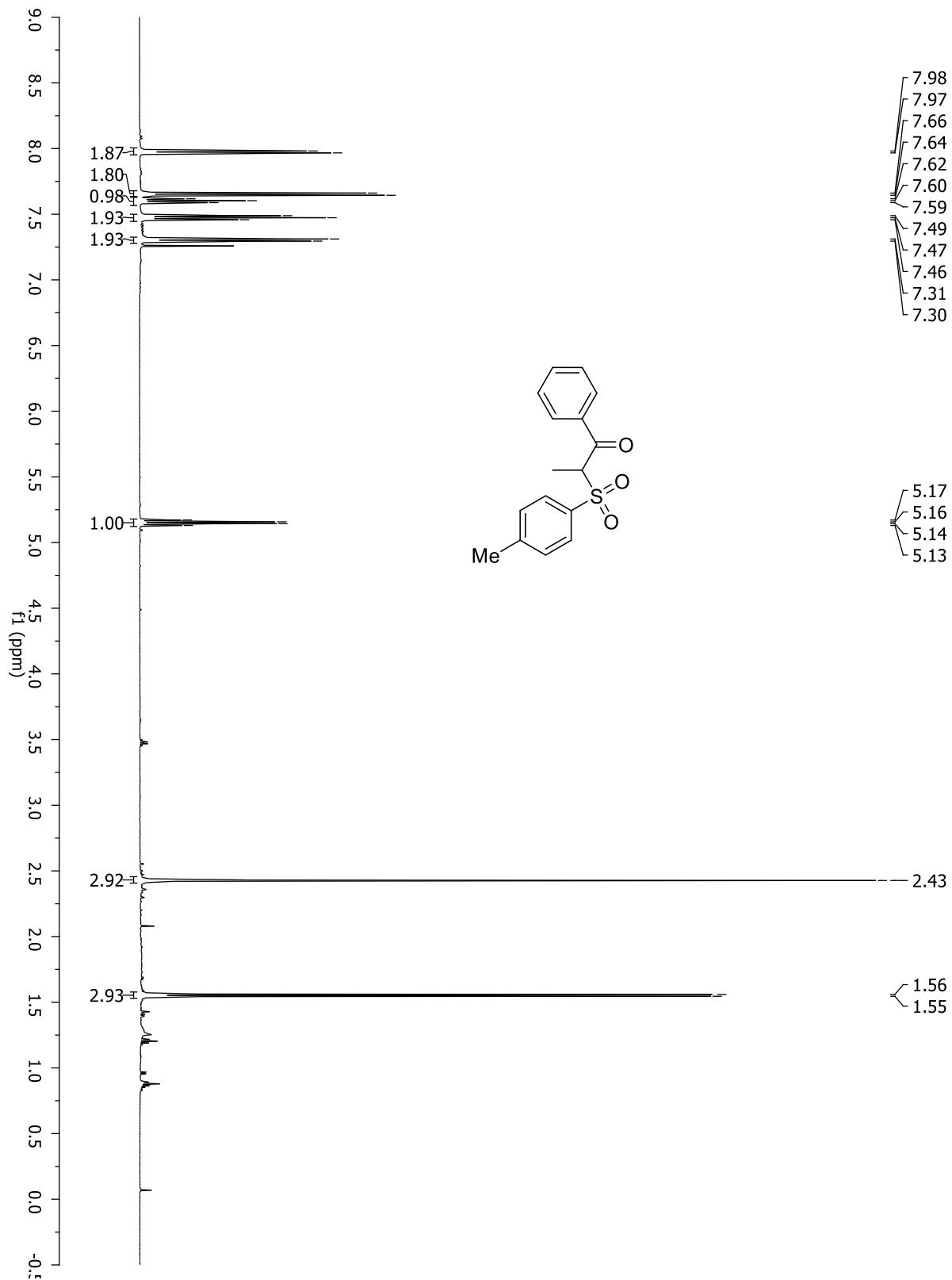
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<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra

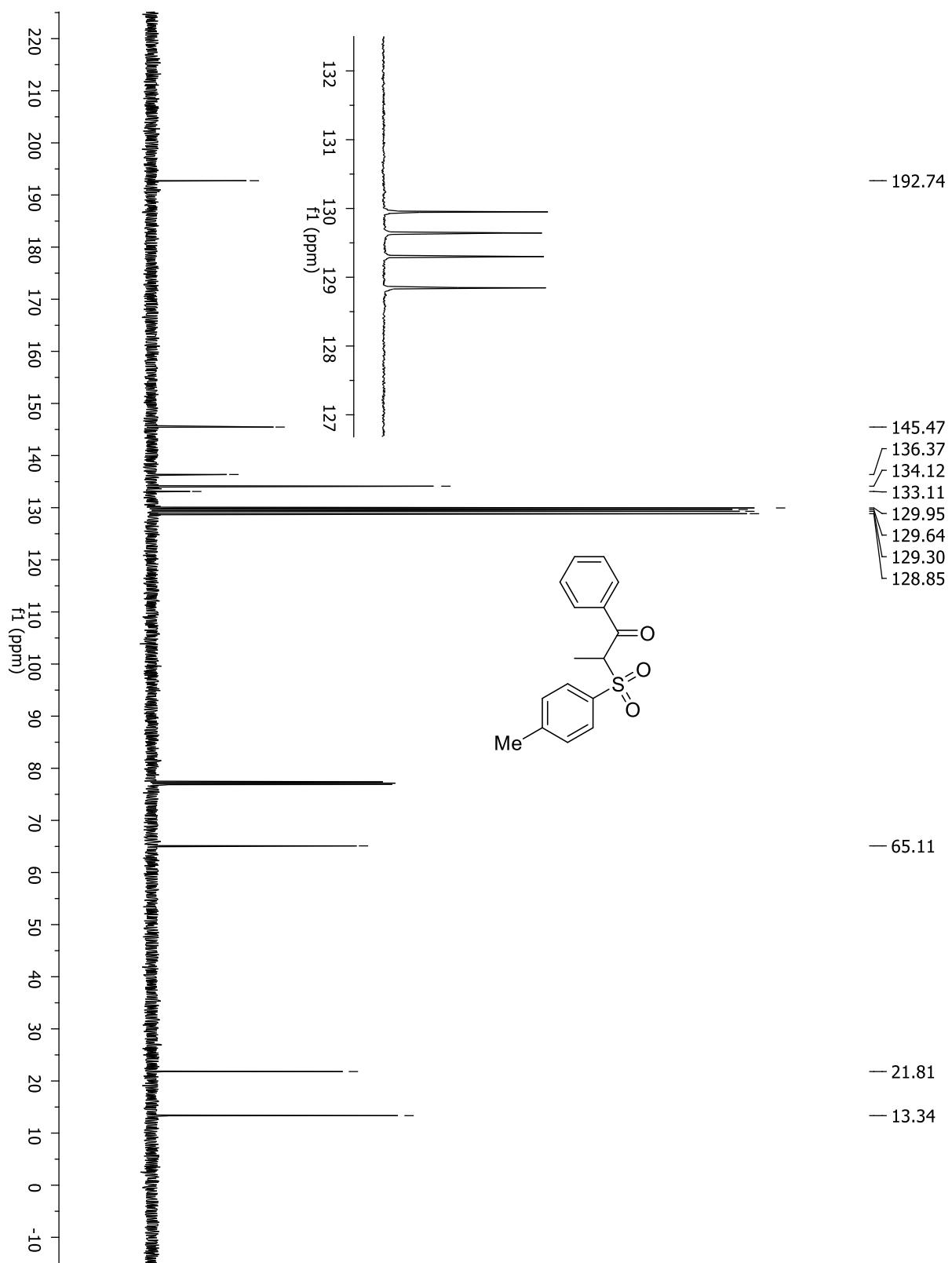
1-Phenyl-2-tosylethanone (3a)



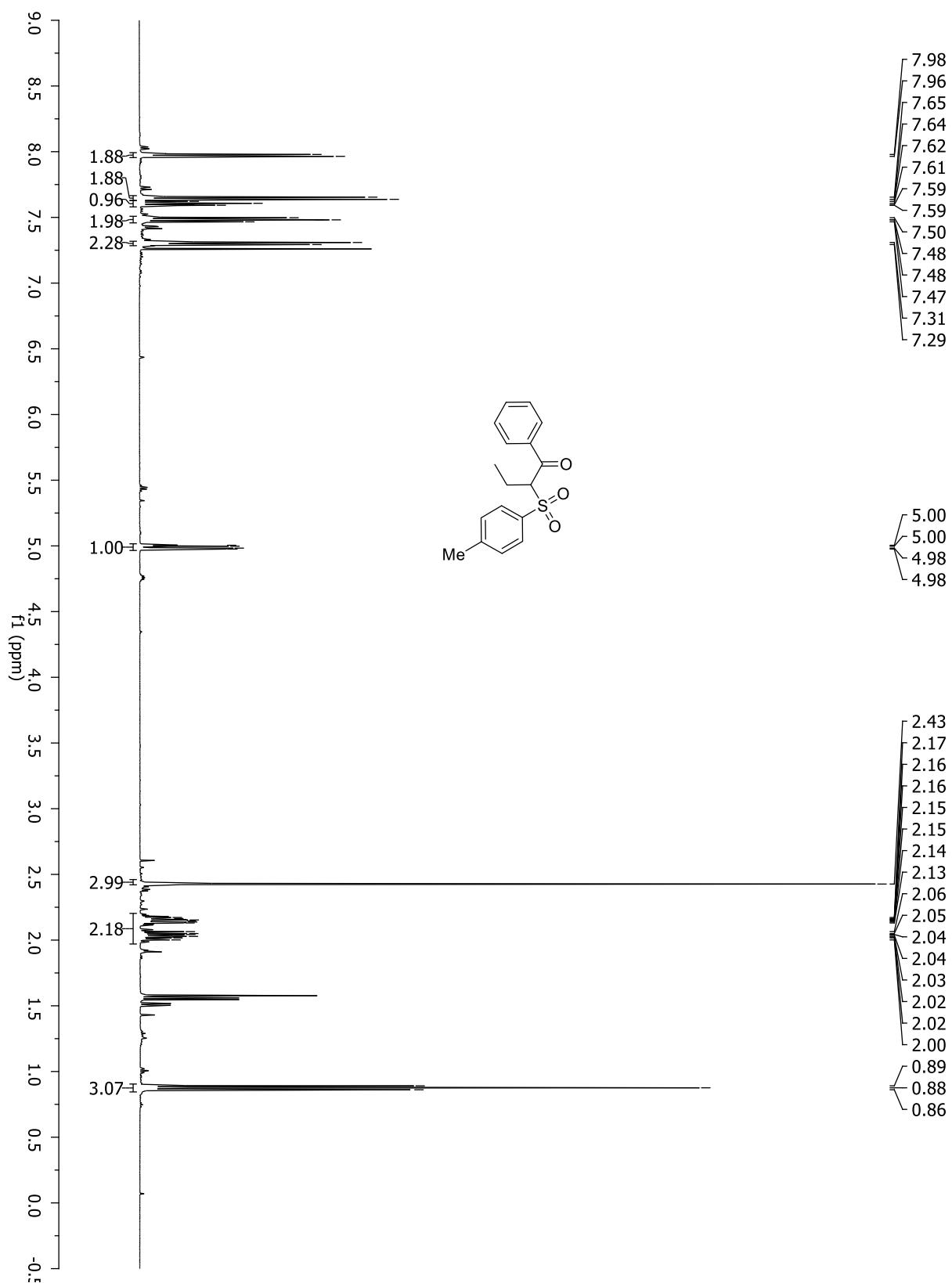
**1-phenyl-2-tosylpropan-1-one (3b)**



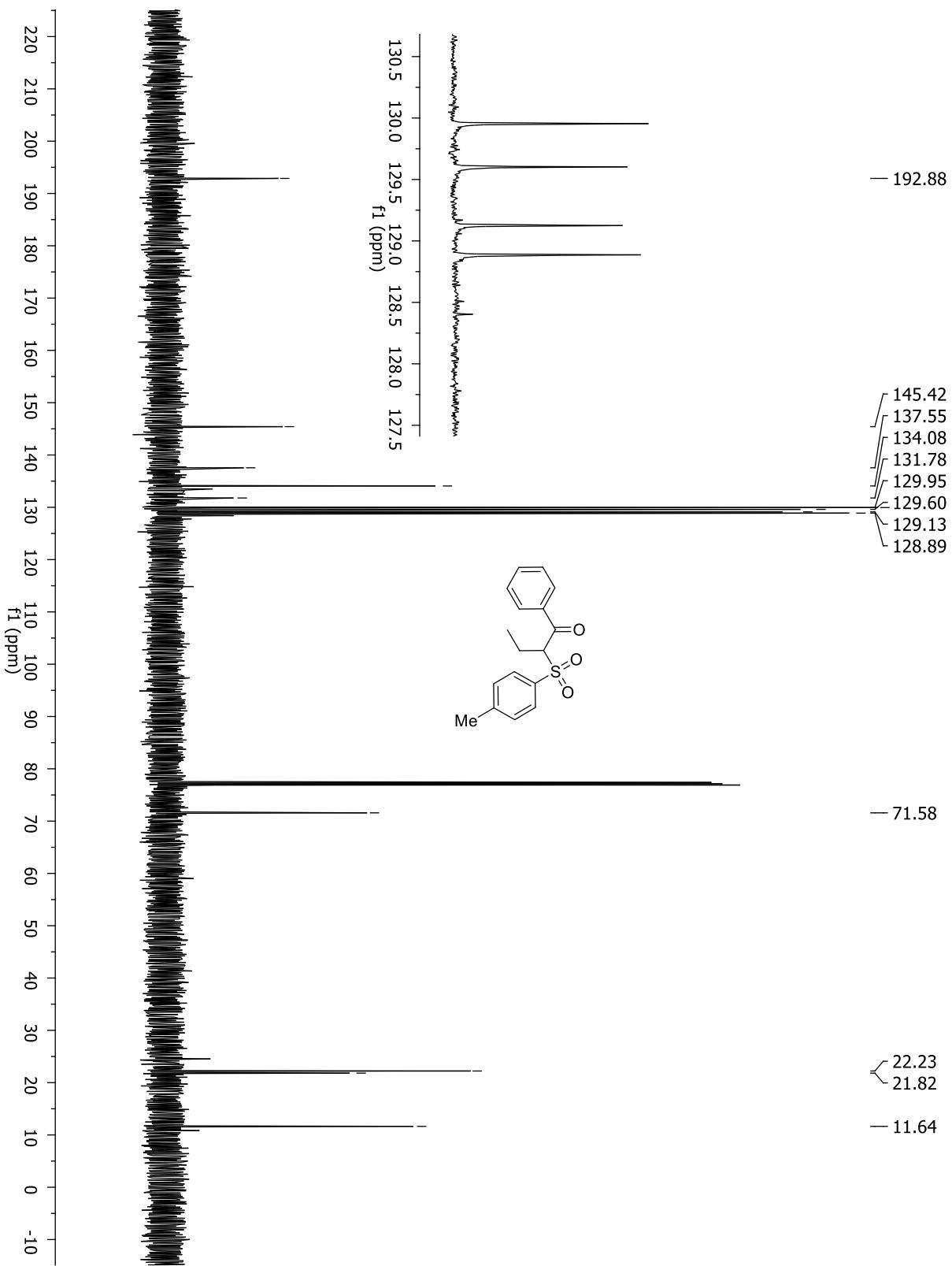
**1-phenyl-2-tosylpropan-1-one (3b)**



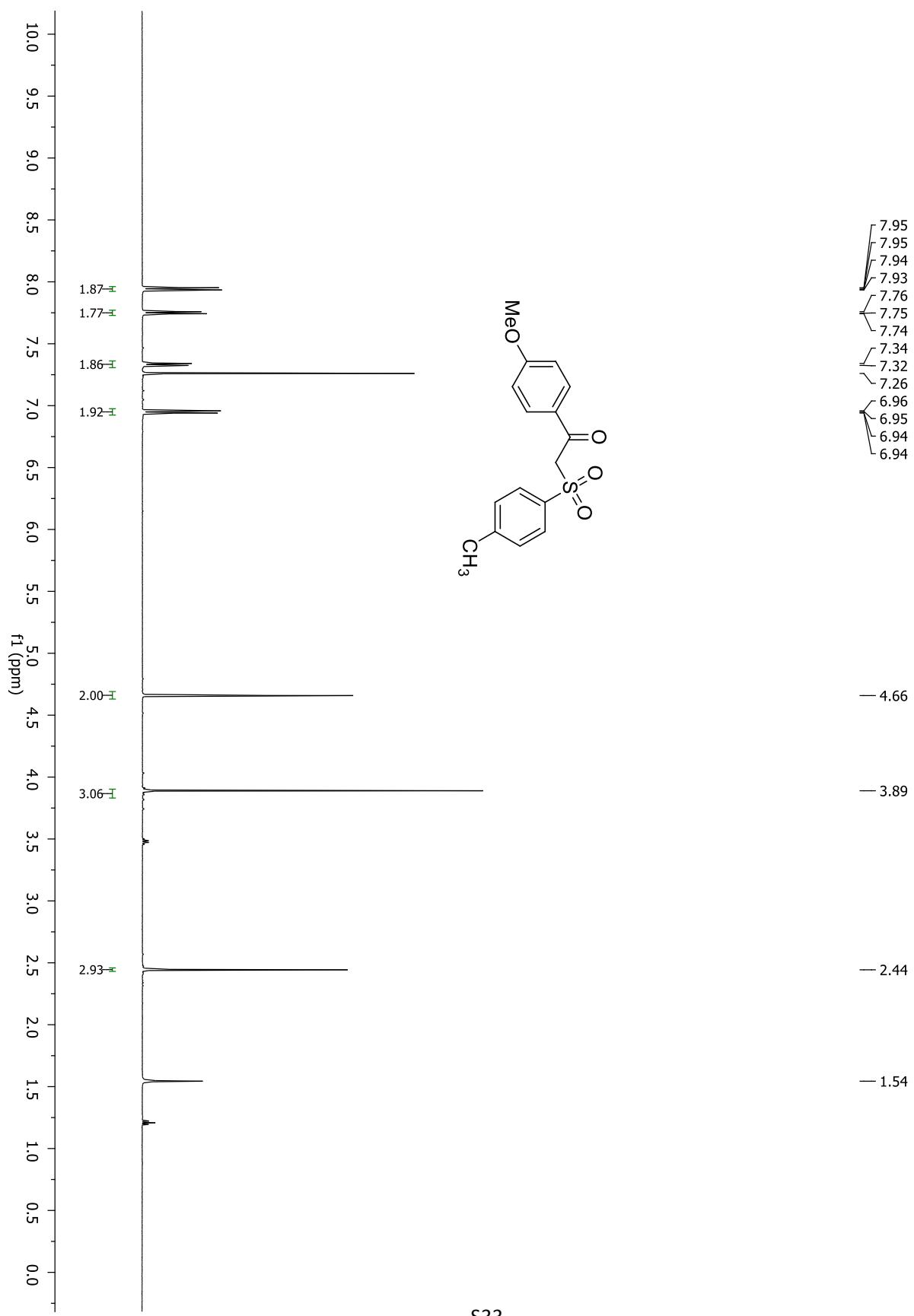
**1-phenyl-2-tosylbutan-1-one (3c)**



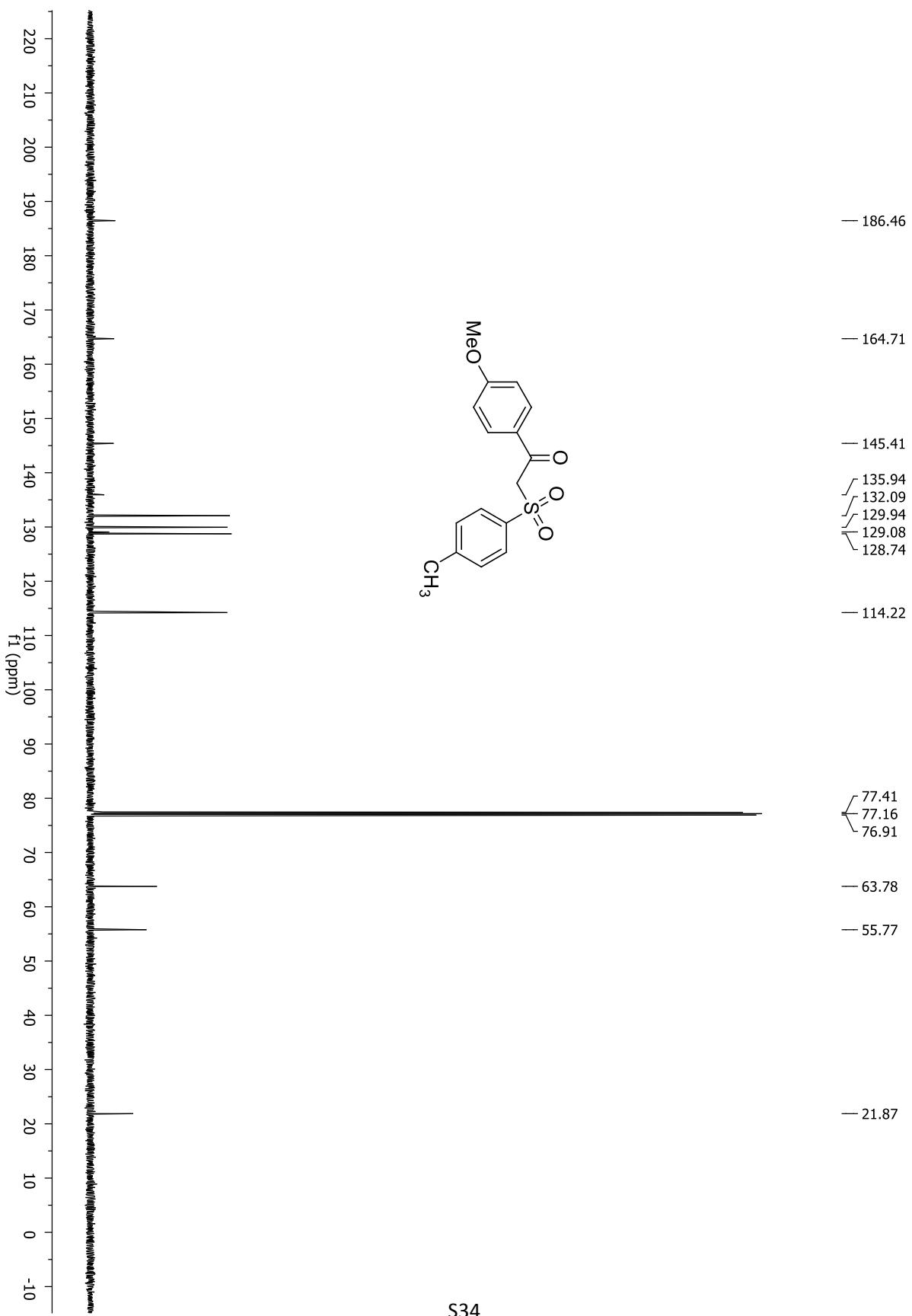
**1-phenyl-2-tosylbutan-1-one (3c)**



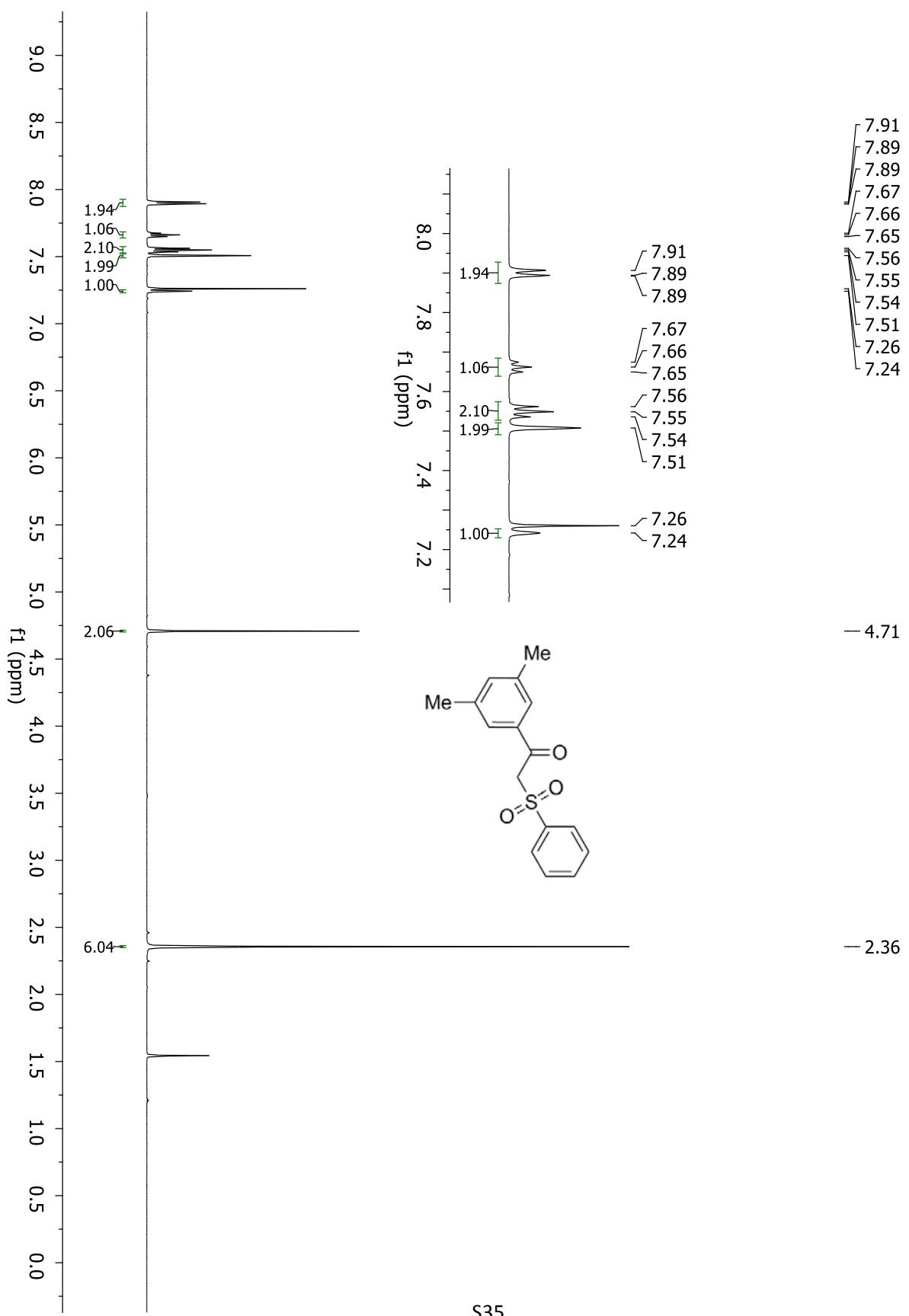
**(4-Methoxyphenyl)-2-tosylethanone (4)**



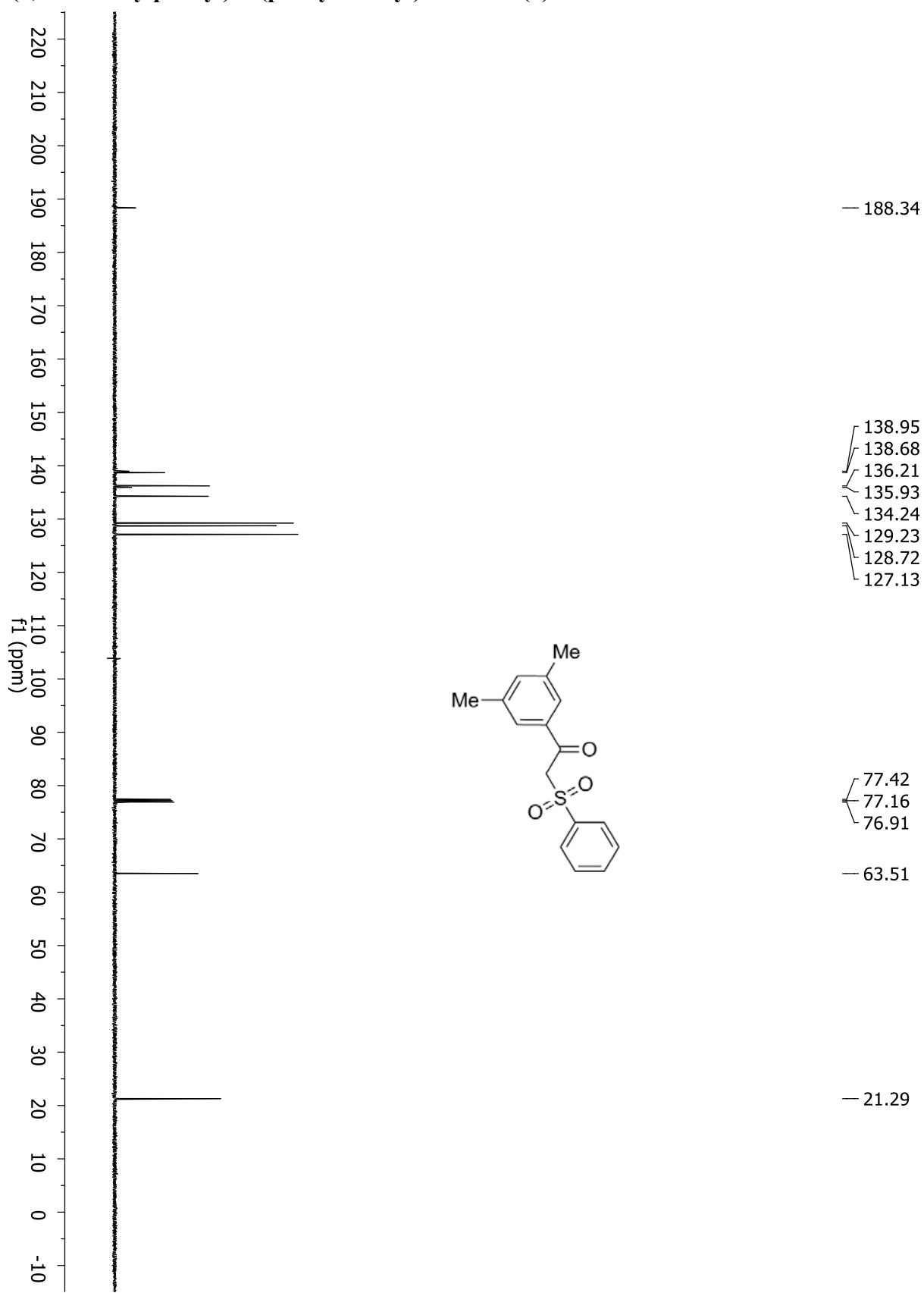
**1-(4-Methoxyphenyl)-2-tosylethanone (4)**



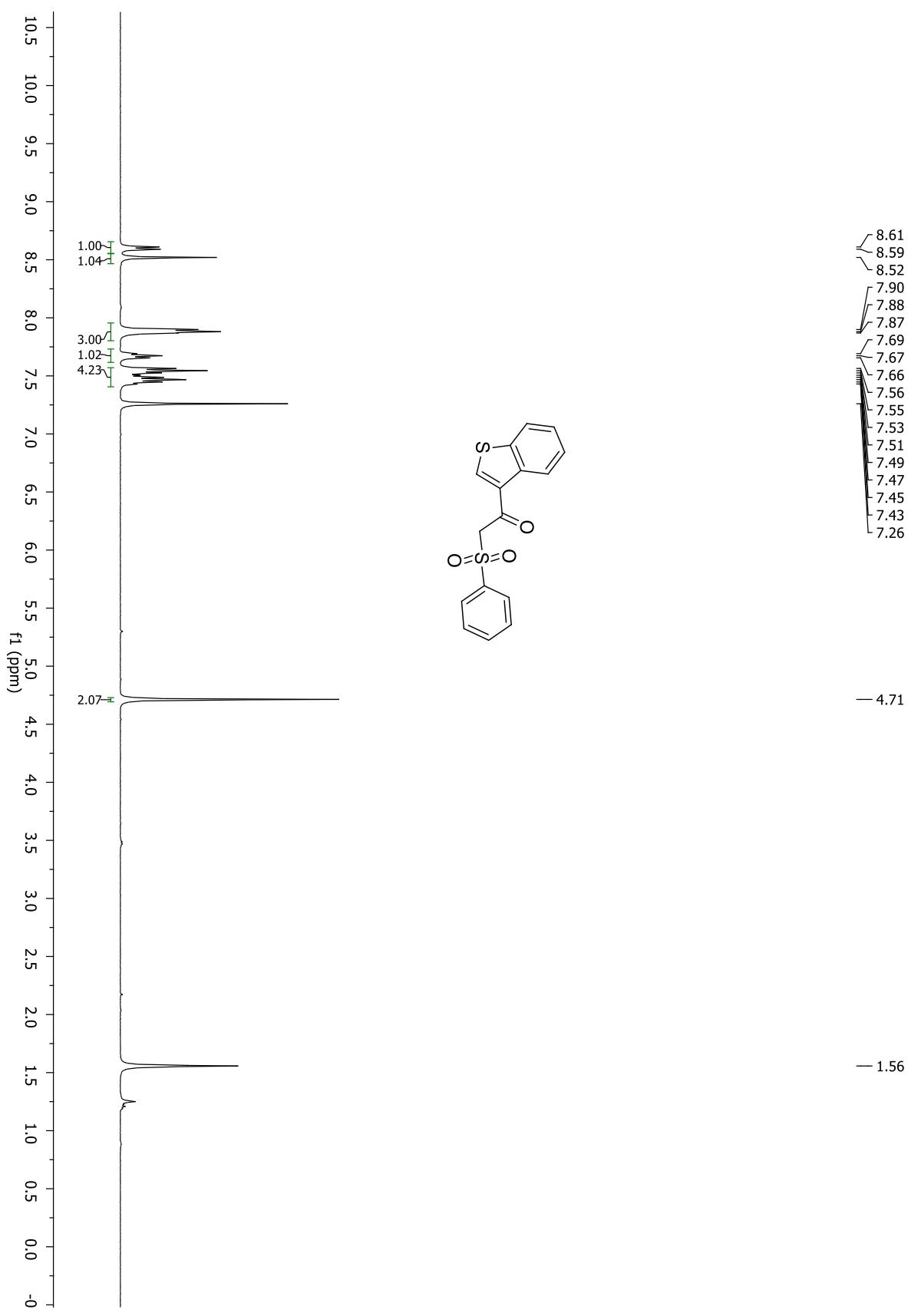
**1-(3,5-Dimethylphenyl)-2-(phenylsulfonyl)ethanone (5)**



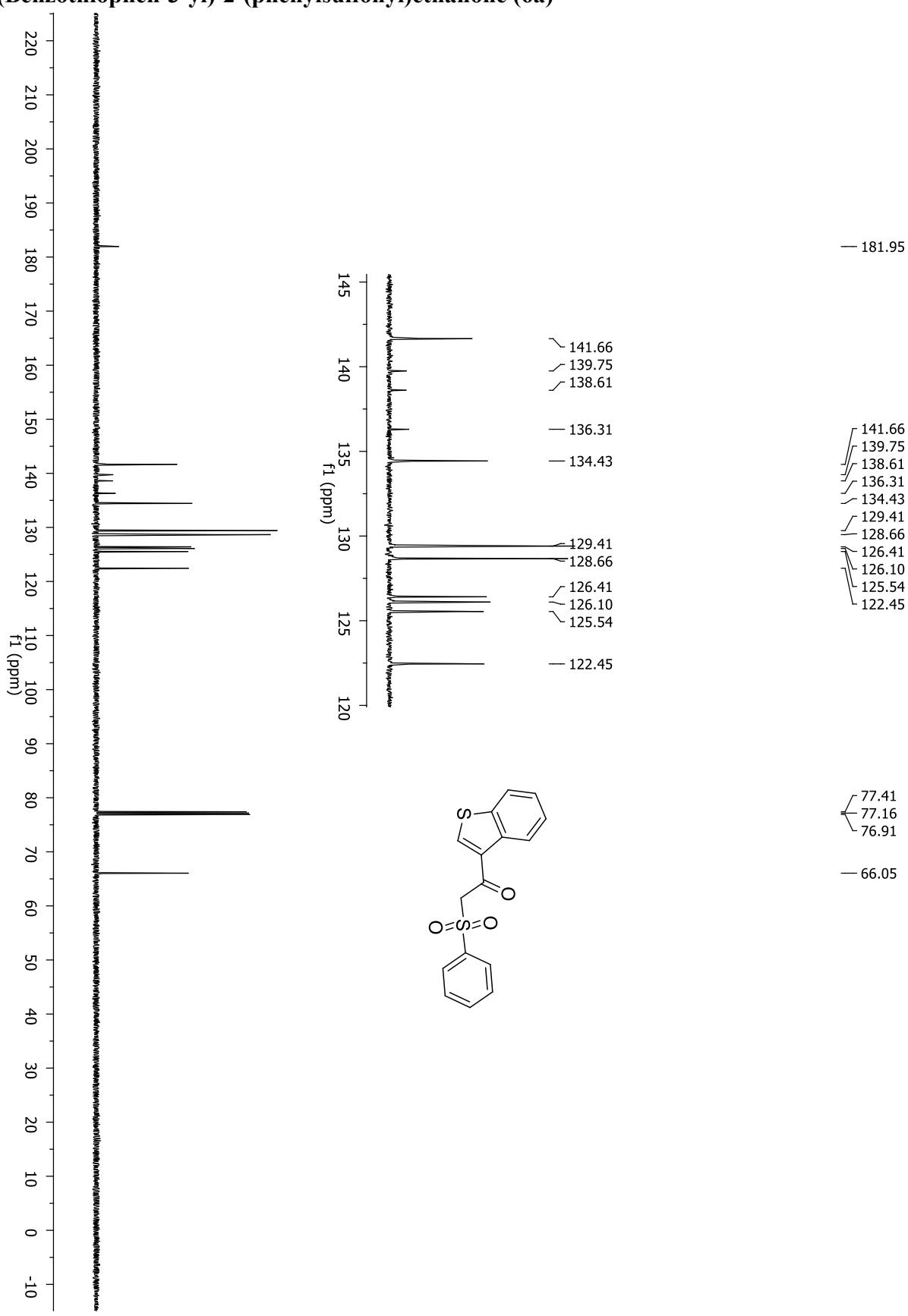
**1-(3,5-Dimethylphenyl)-2-(phenylsulfonyl)ethanone (5)**



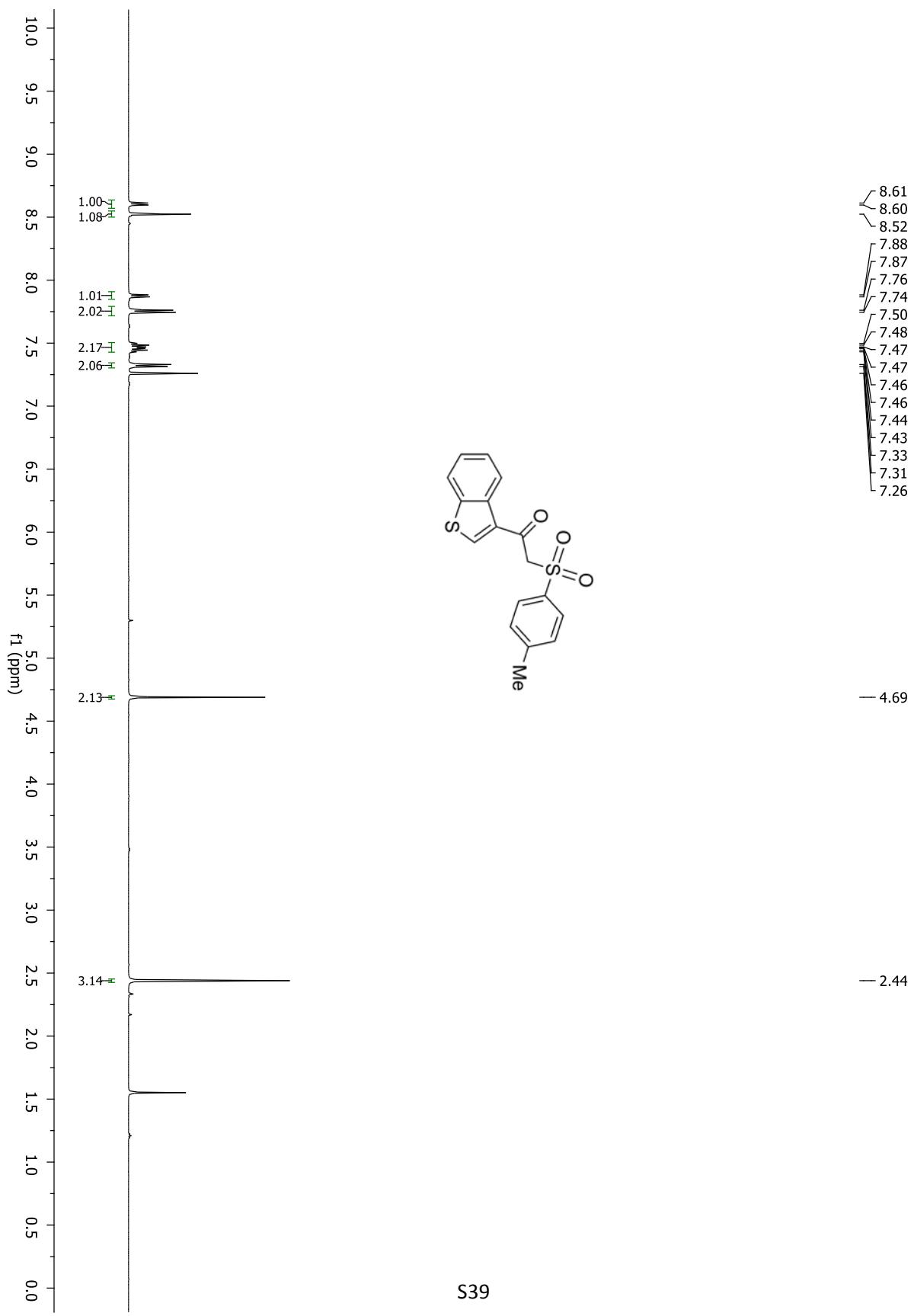
**1-(Benzothiophen-3-yl)-2-(phenylsulfonyl)ethanone (6a)**



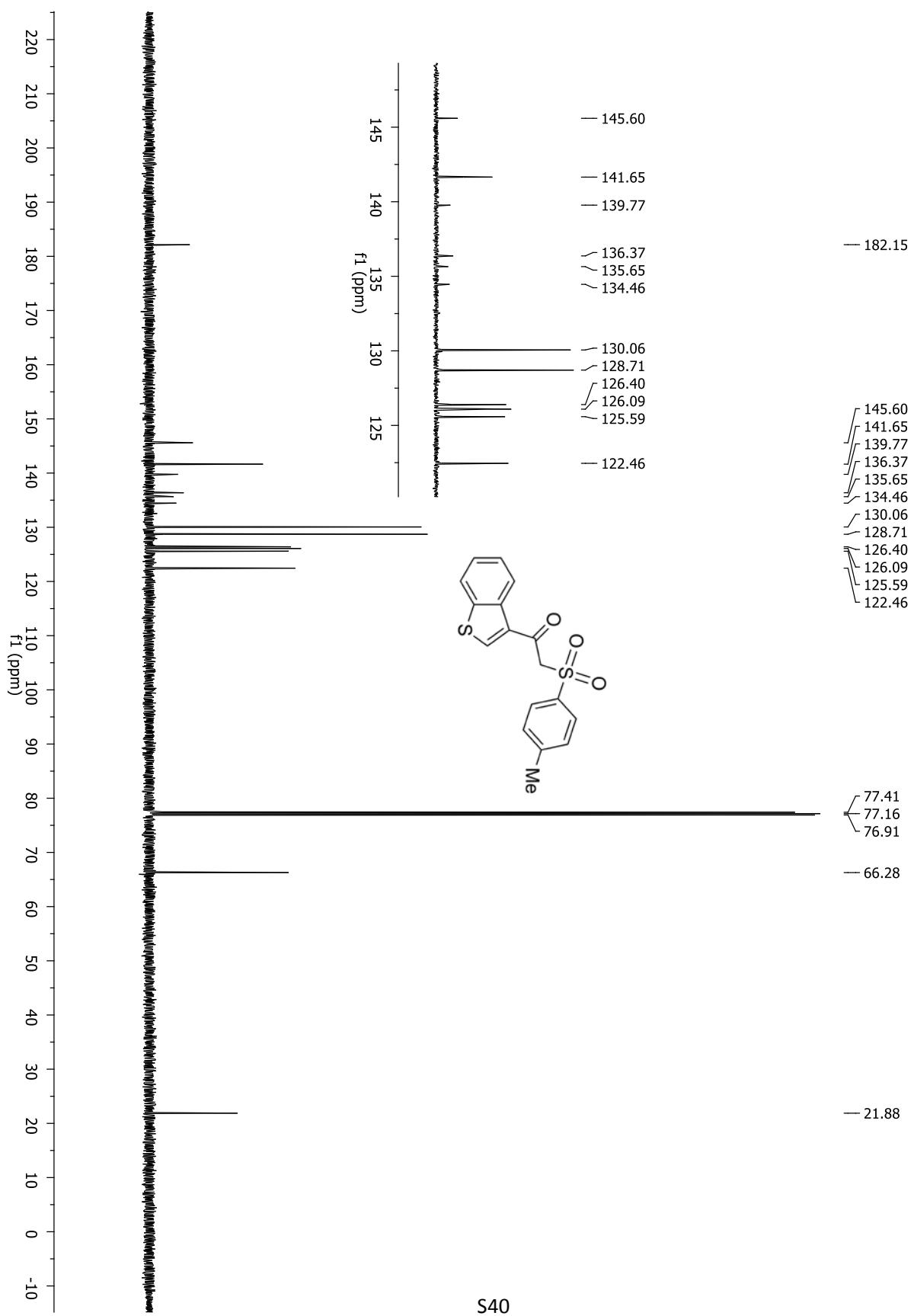
**1-(Benzothiophen-3-yl)-2-(phenylsulfonyl)ethanone (6a)**



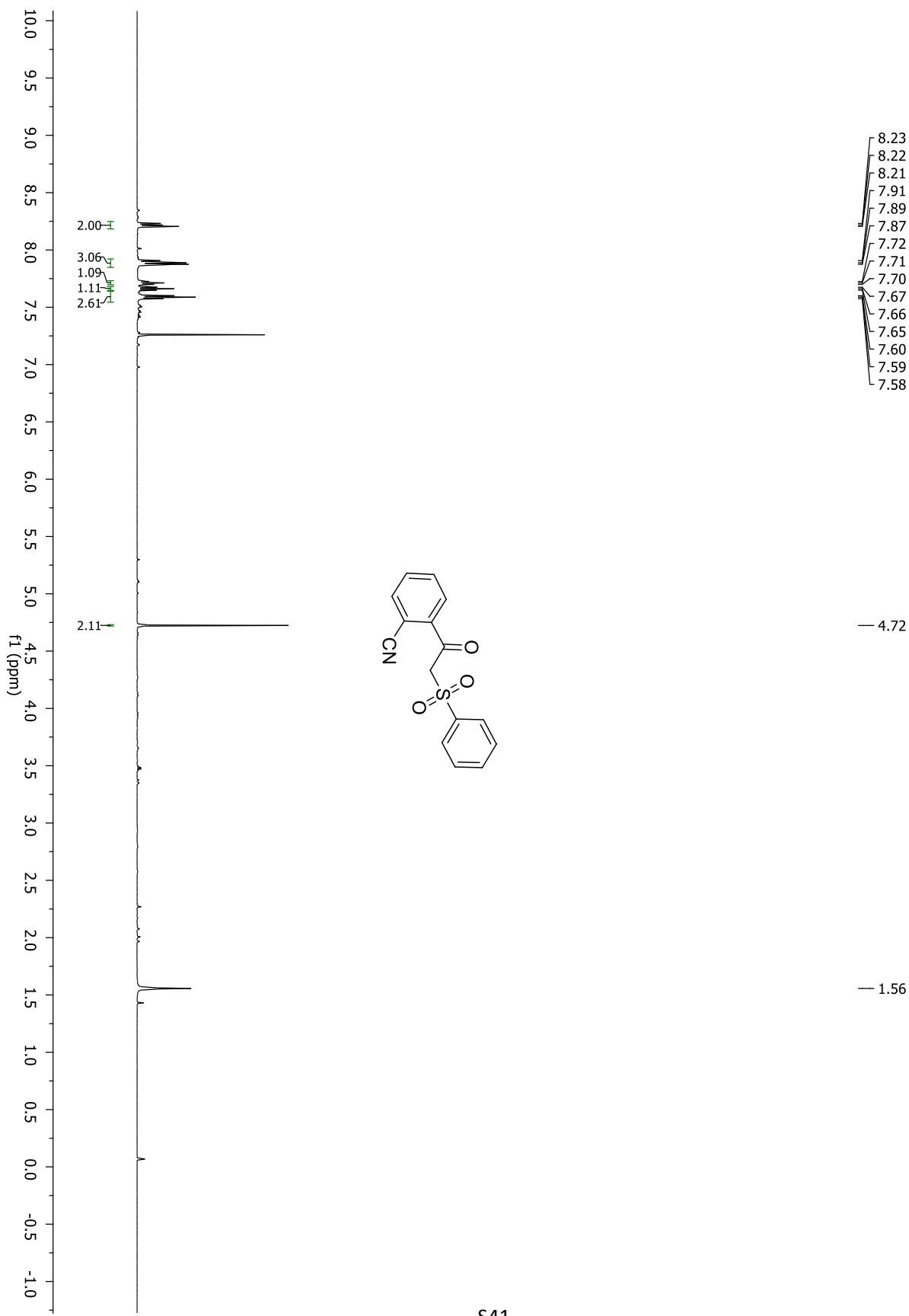
**1-(Benzothiophen-3-yl)-2-tosylethanone (6b)**



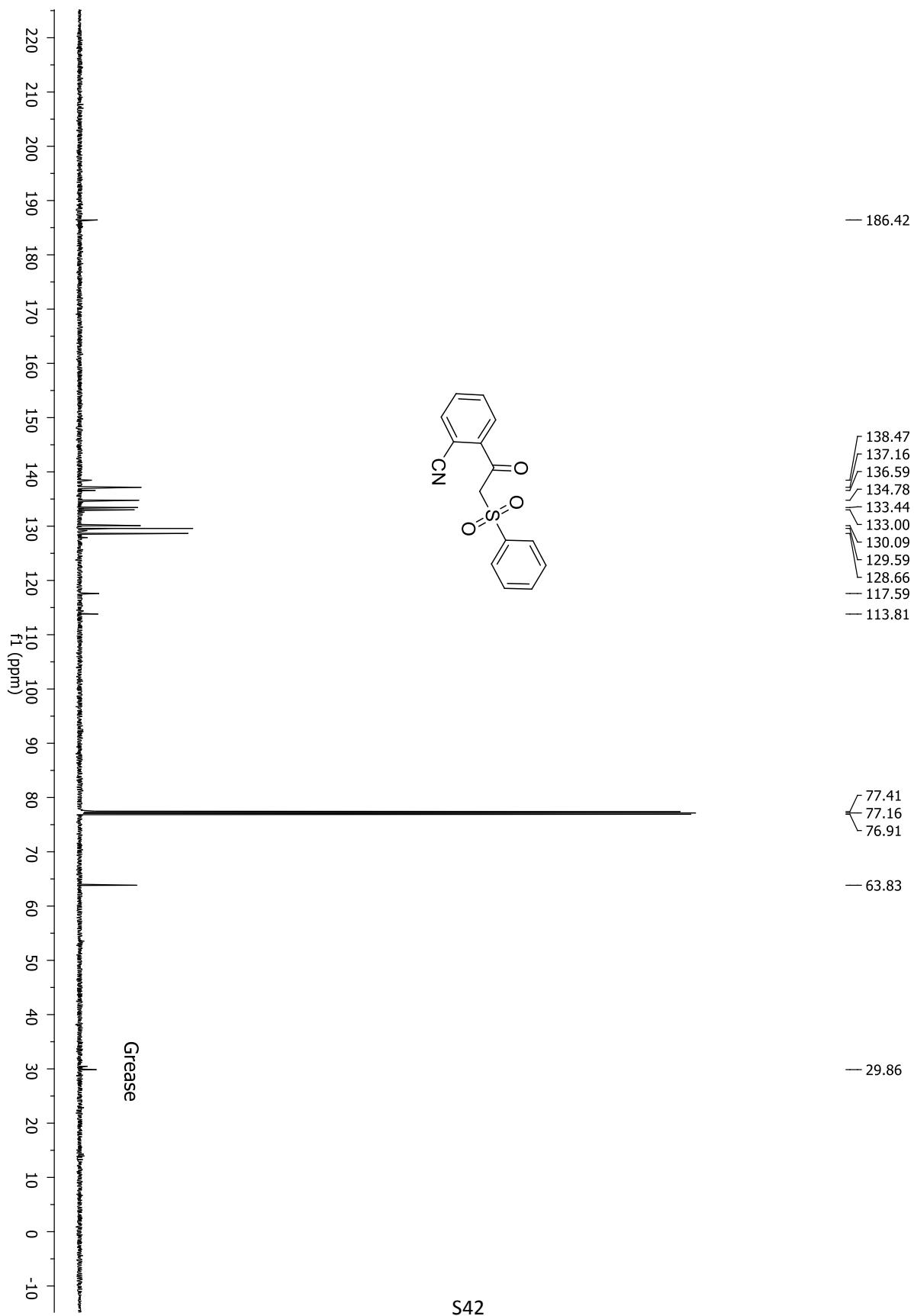
**1-(Benzothiophen-3-yl)-2-tosylethanone (6b)**



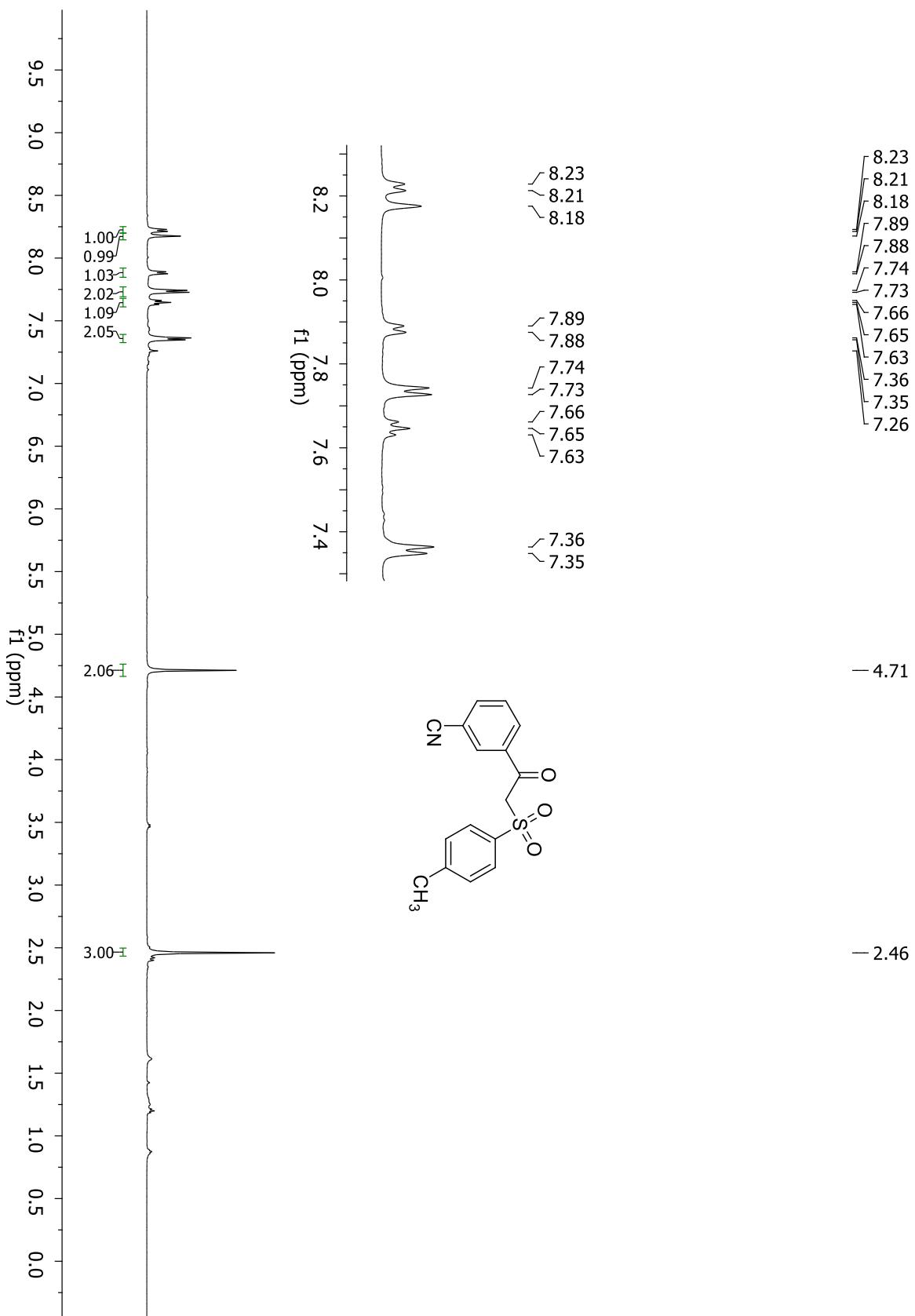
**3-(2-(Phenethylsulfonyl)acetyl)benzonitrile (7)**



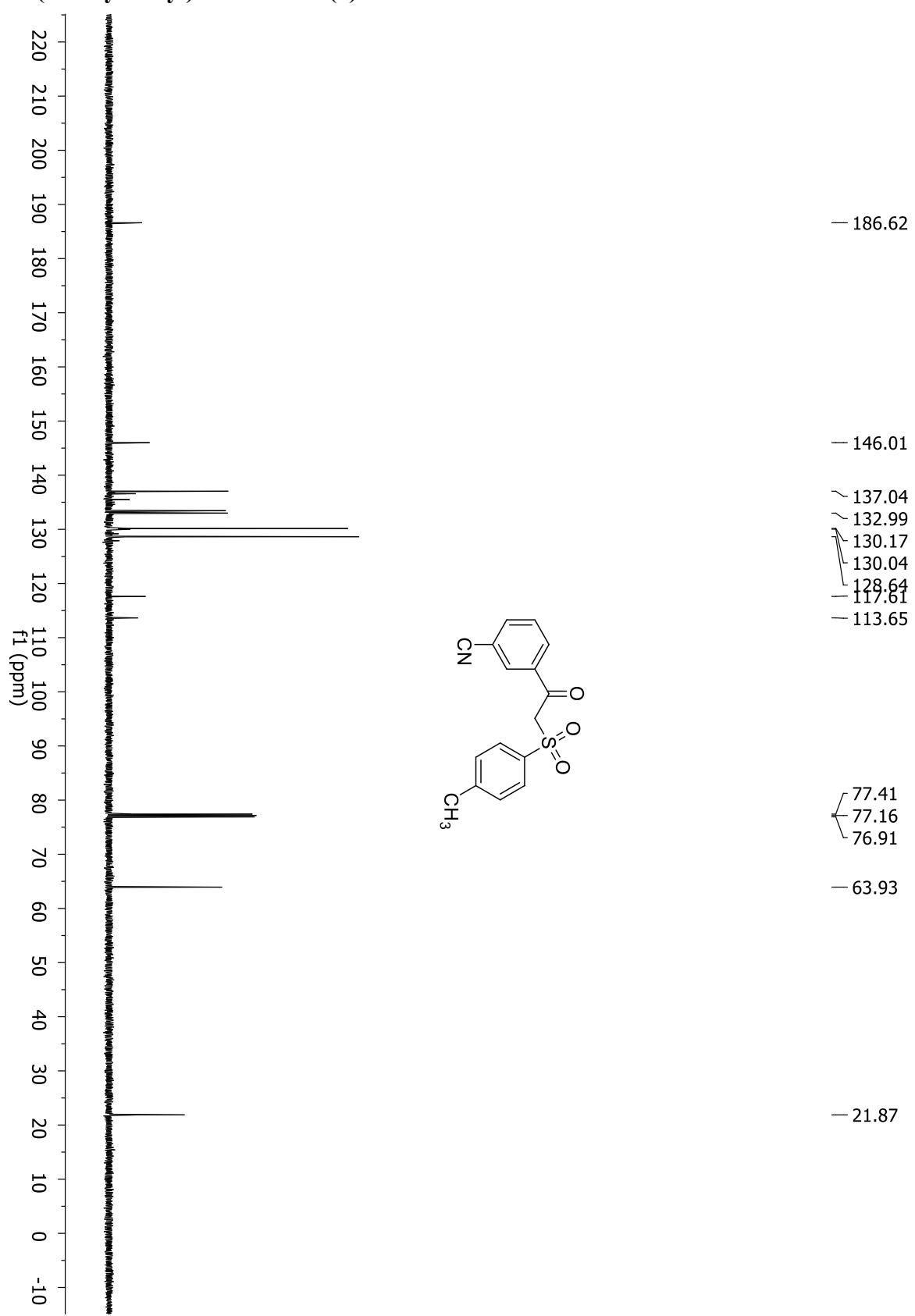
**3-(2-(Phenethylsulfonyl)acetyl)benzonitrile (7)**



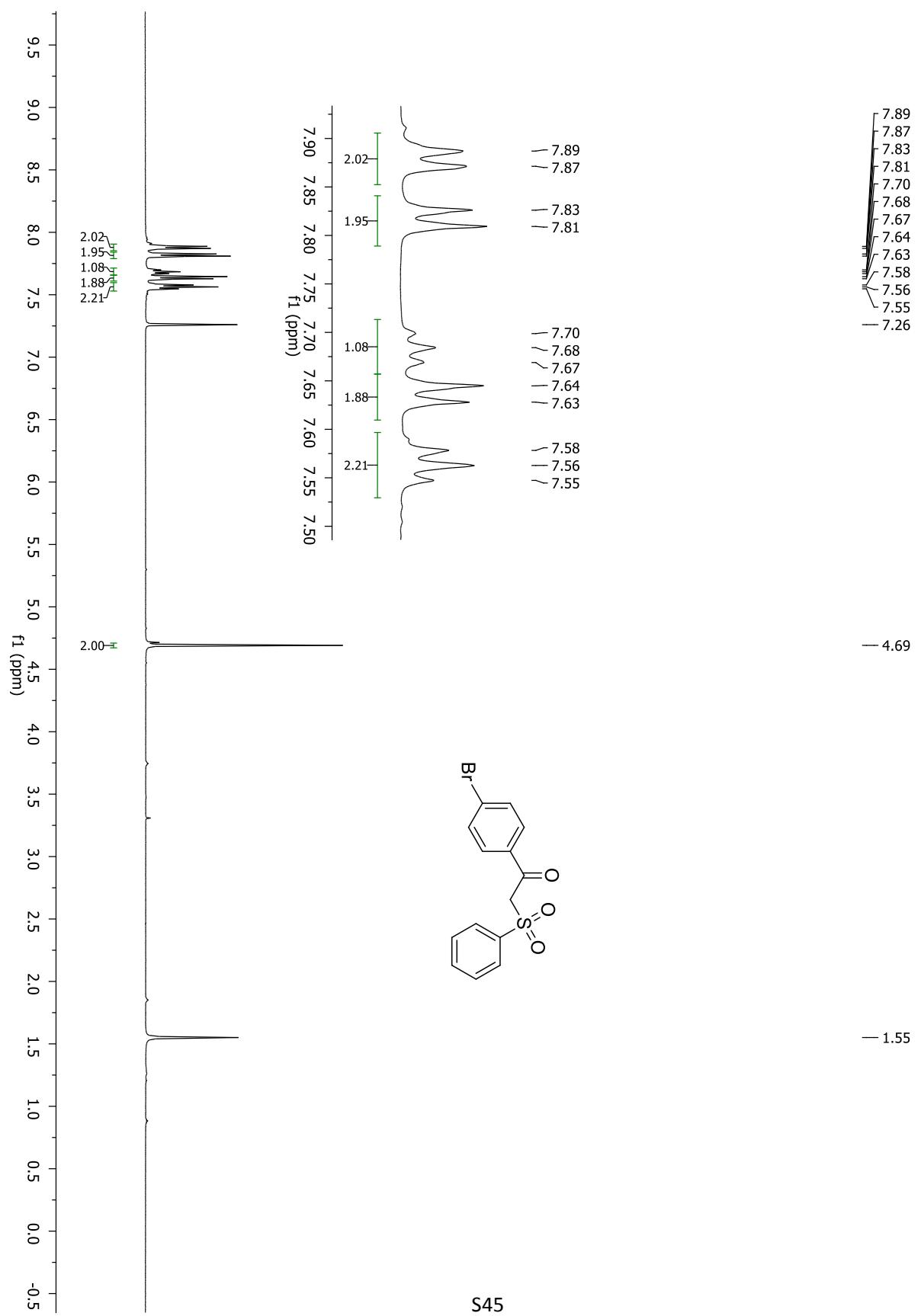
**3-(2-Tosylacetyl)benzonitrile (8)**



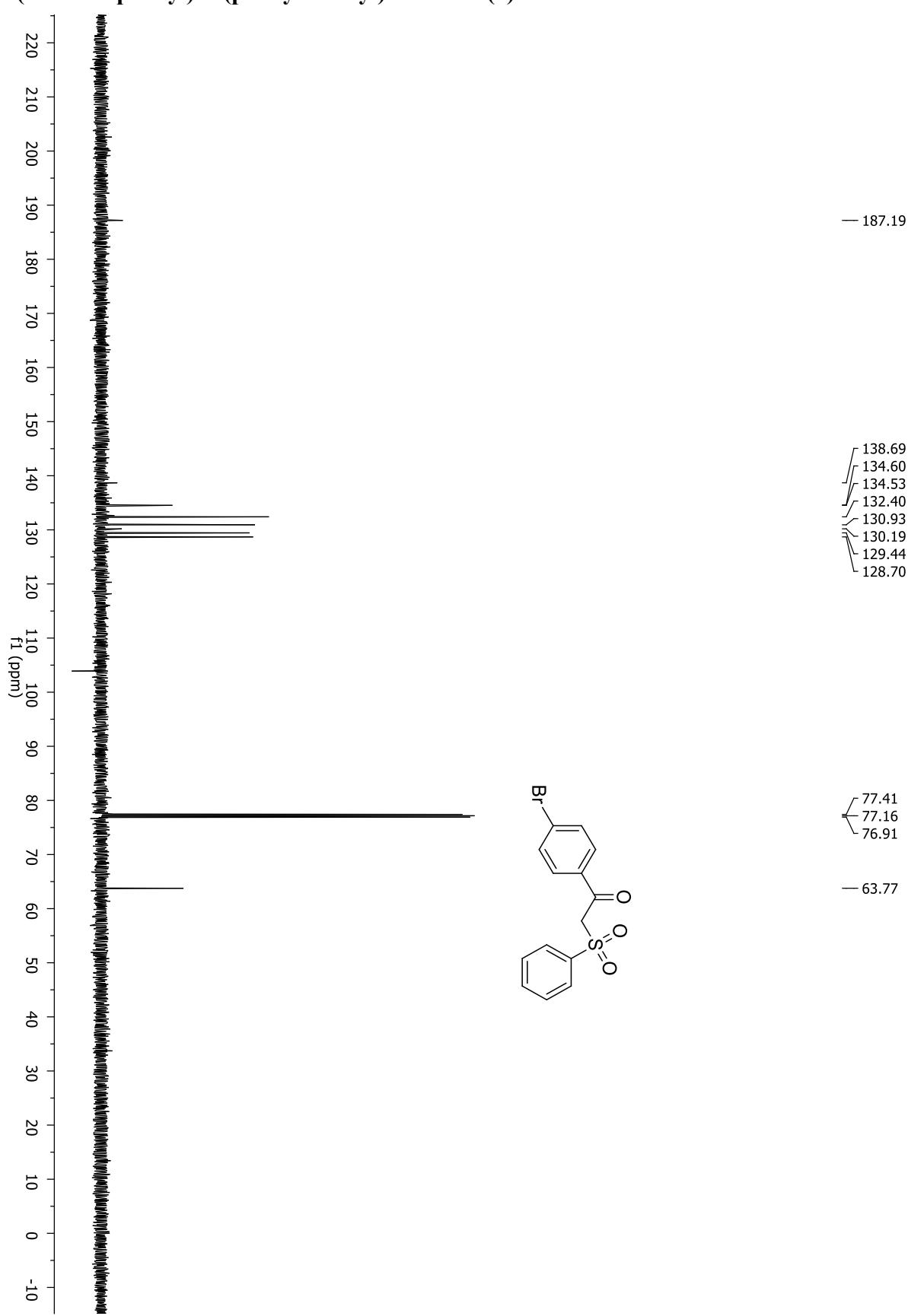
**3-(2-Tosylacetyl)benzonitrile (8)**



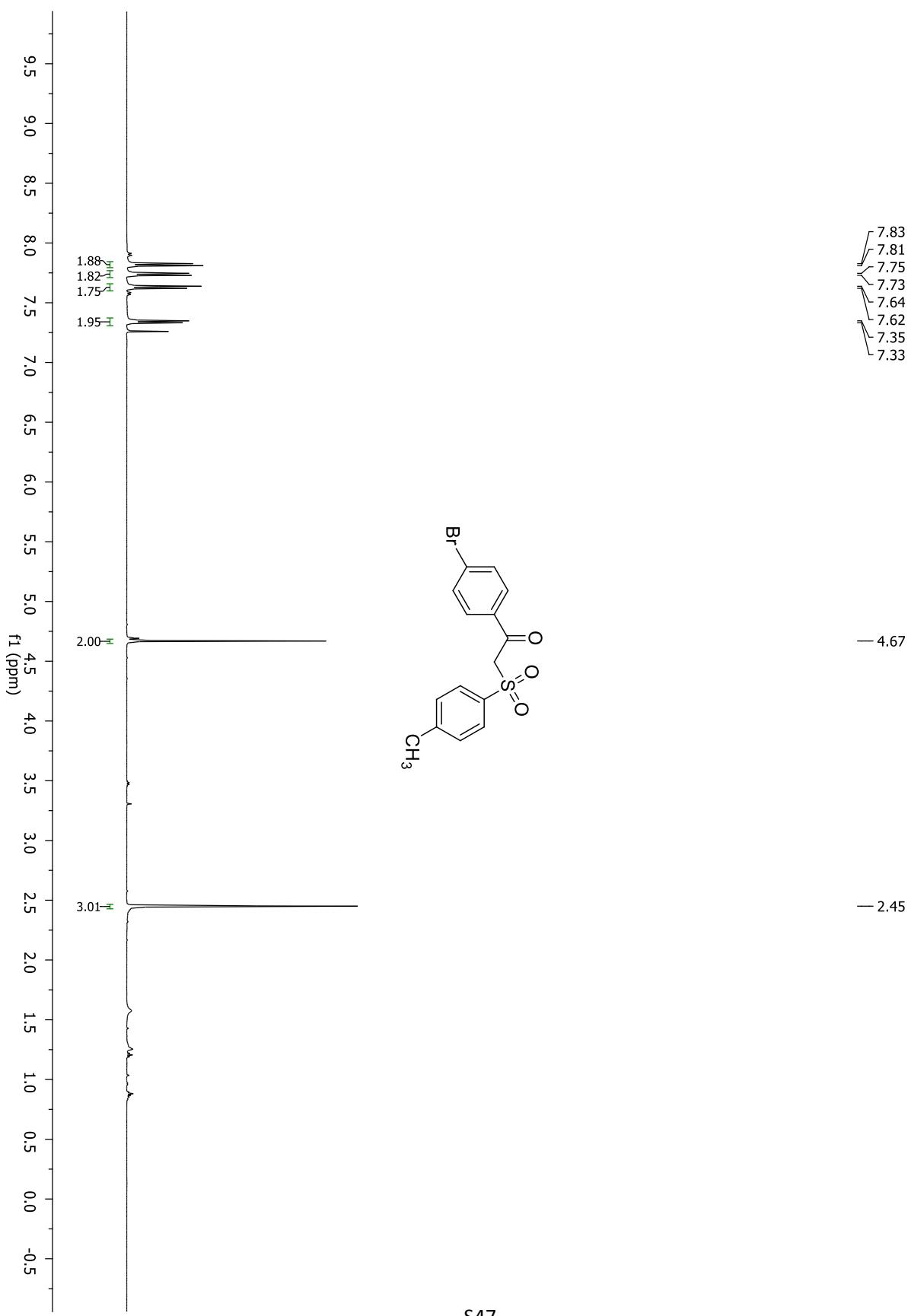
**1-(4-Bromophenyl)-2-(phenylsulfonyl)ethanone (9)**



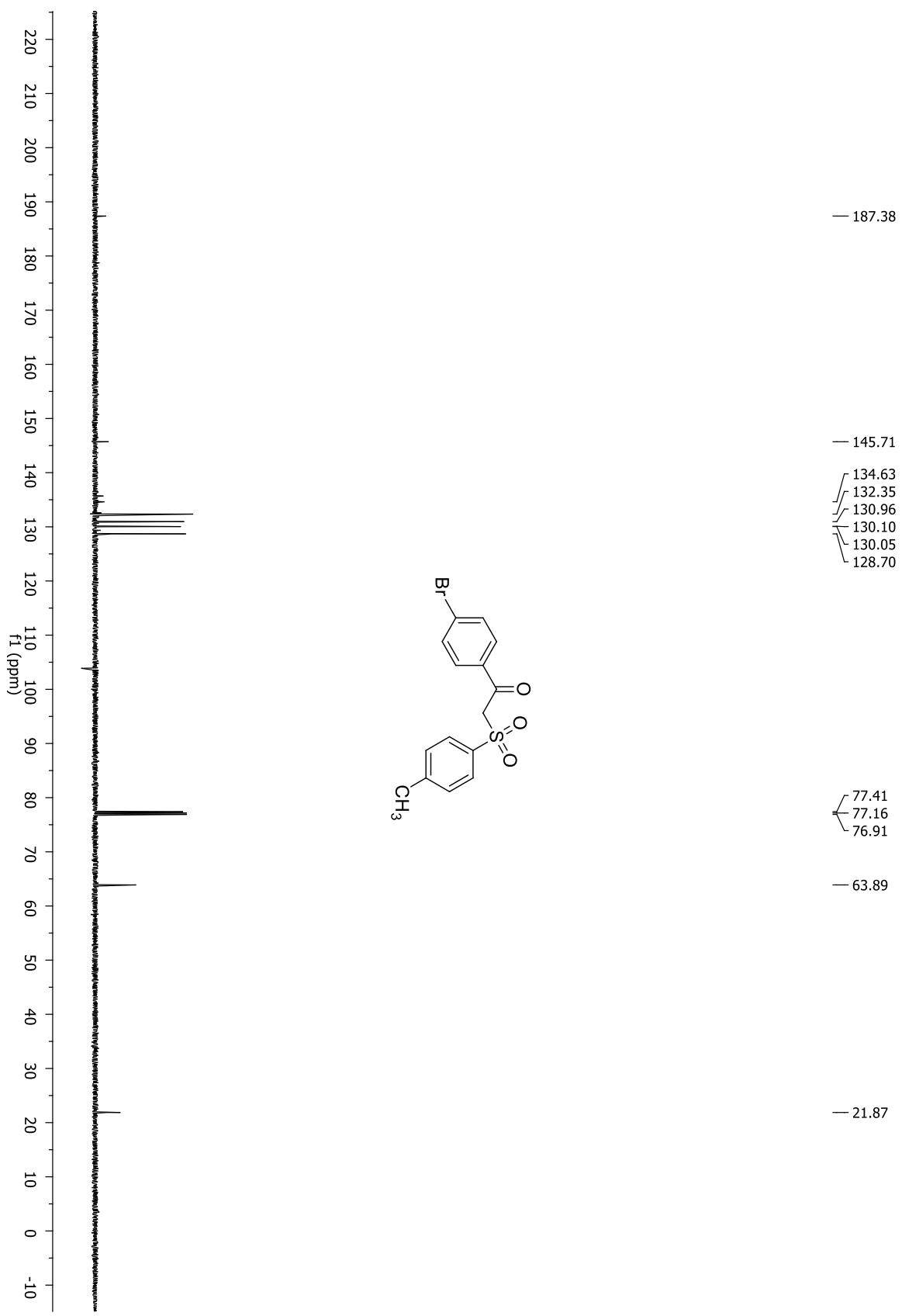
**1-(4-Bromophenyl)-2-(phenylsulfonyl)ethanone (9)**



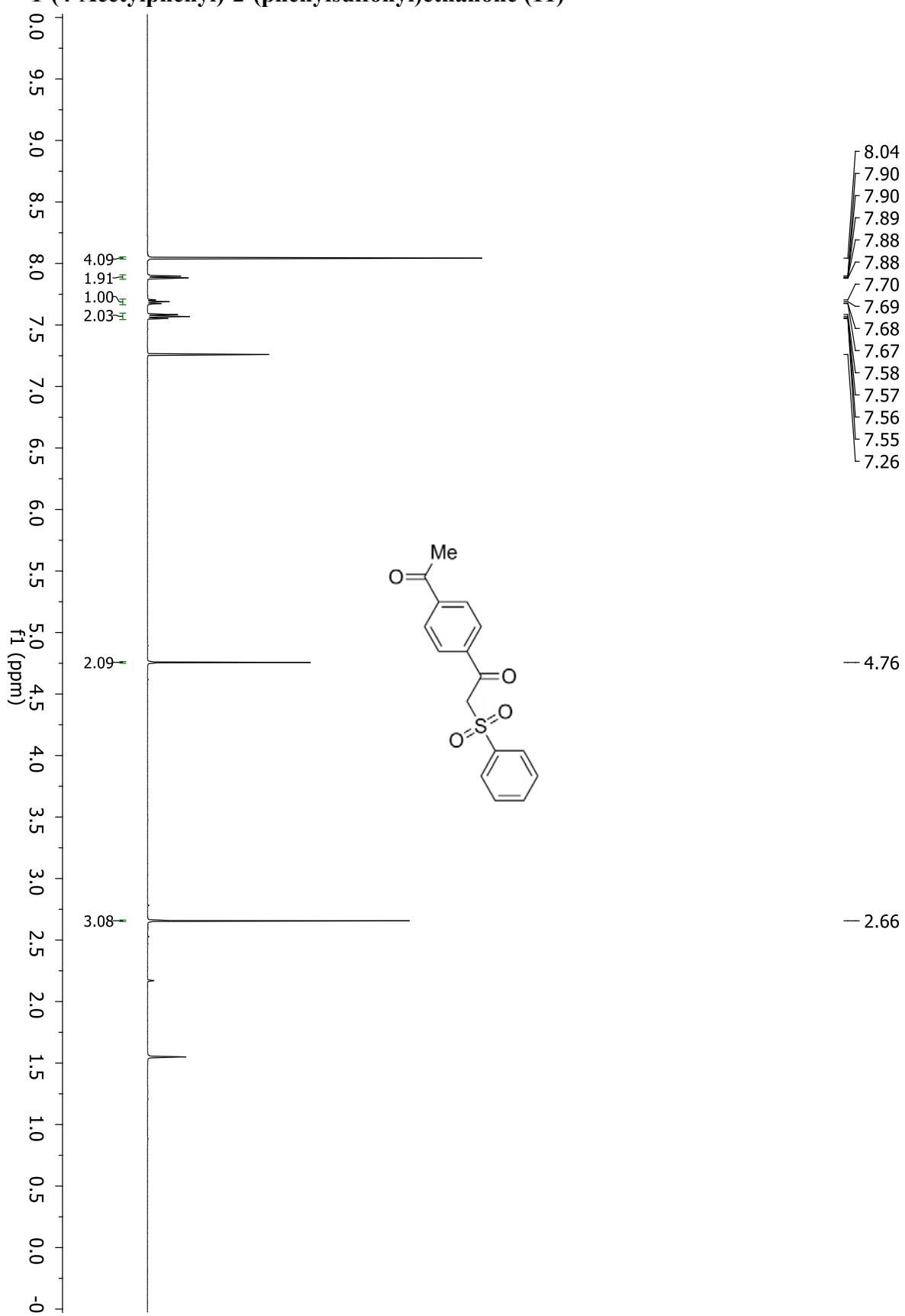
**1-(4-Bromophenyl)-2-tosylethanone (10)**



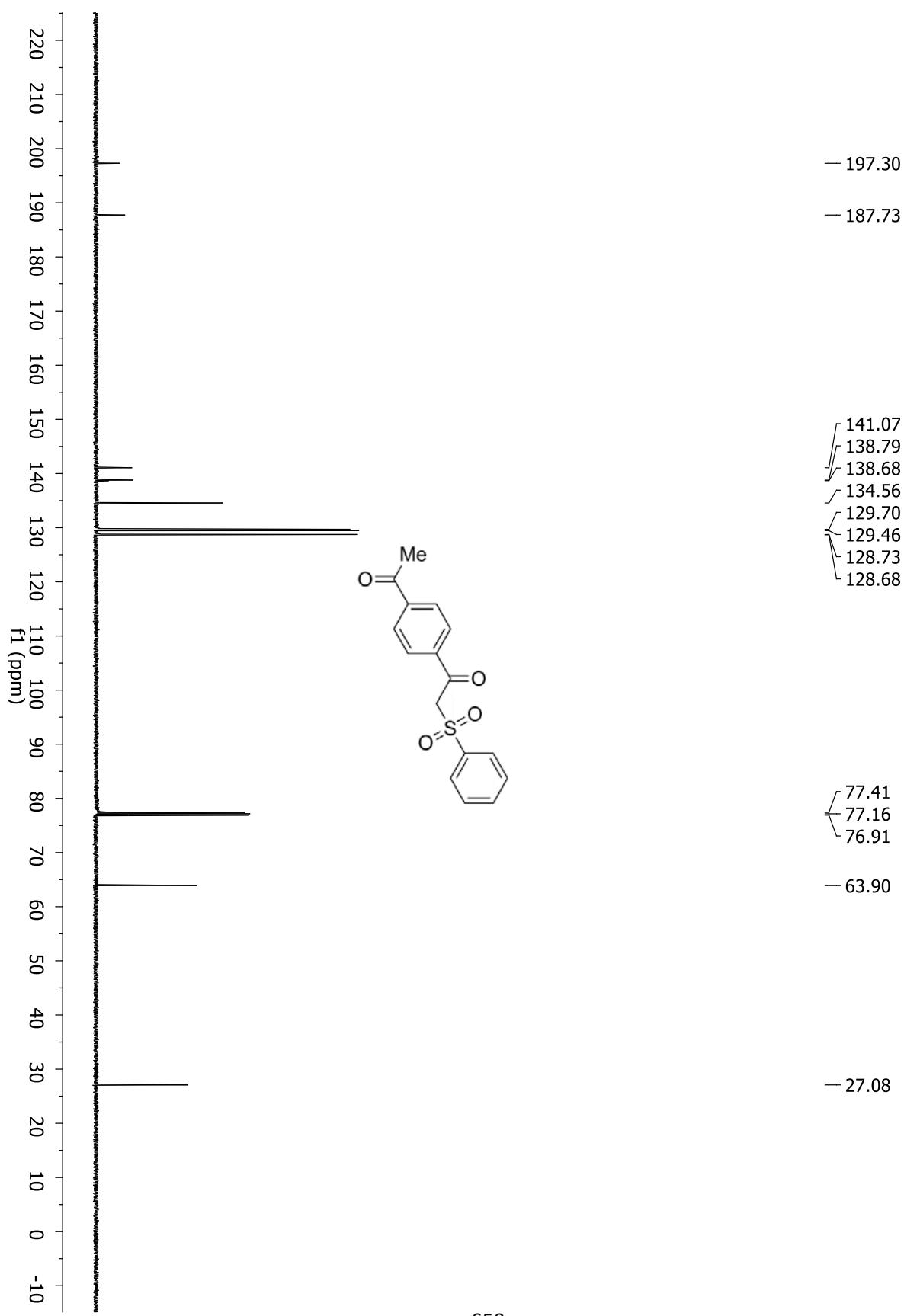
**1-(4-Bromophenyl)-2-tosylethanone (10)**



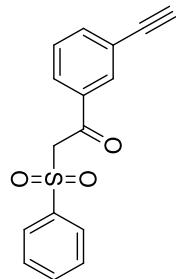
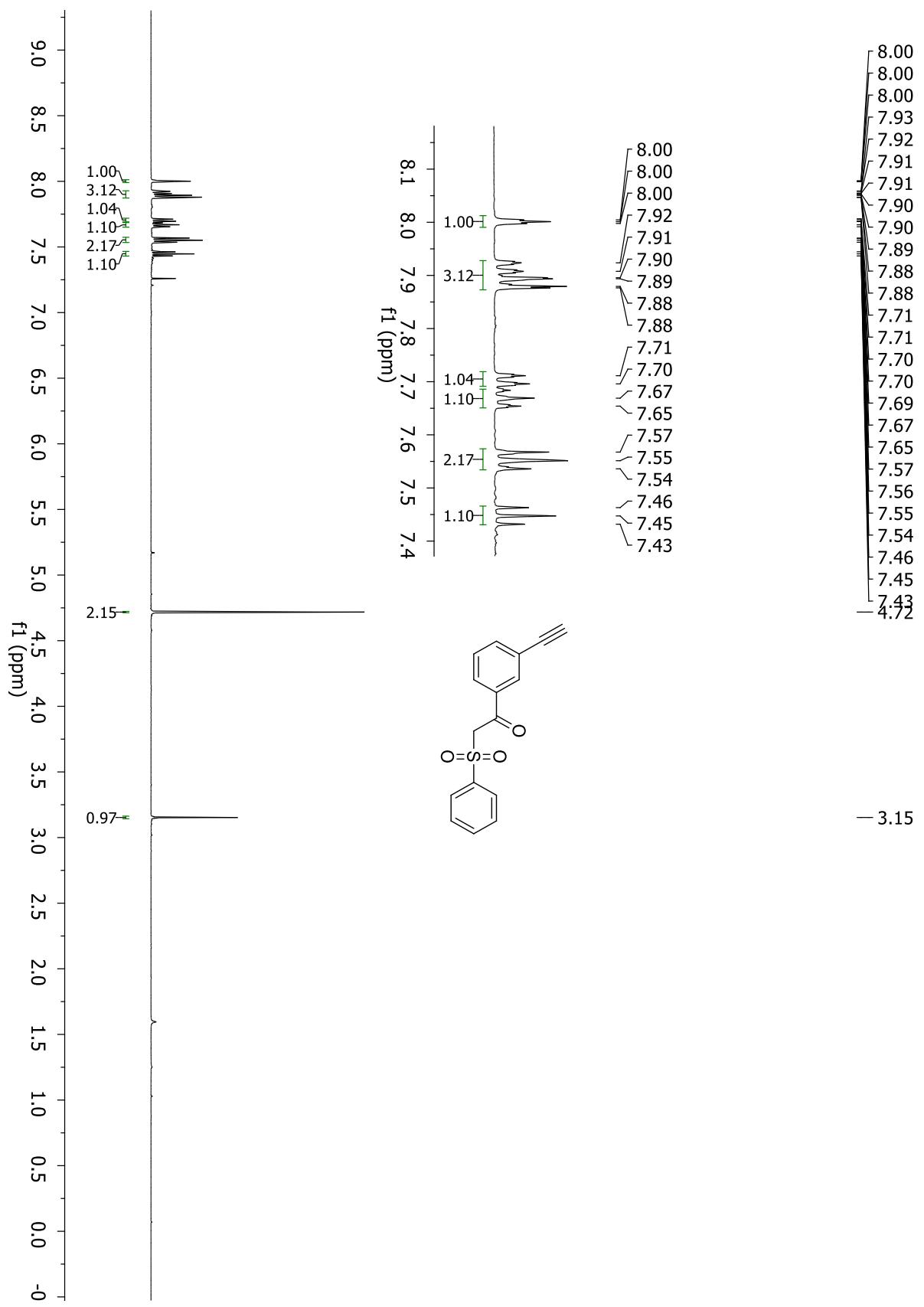
**1-(4-Acetylphenyl)-2-(phenylsulfonyl)ethanone (11)**



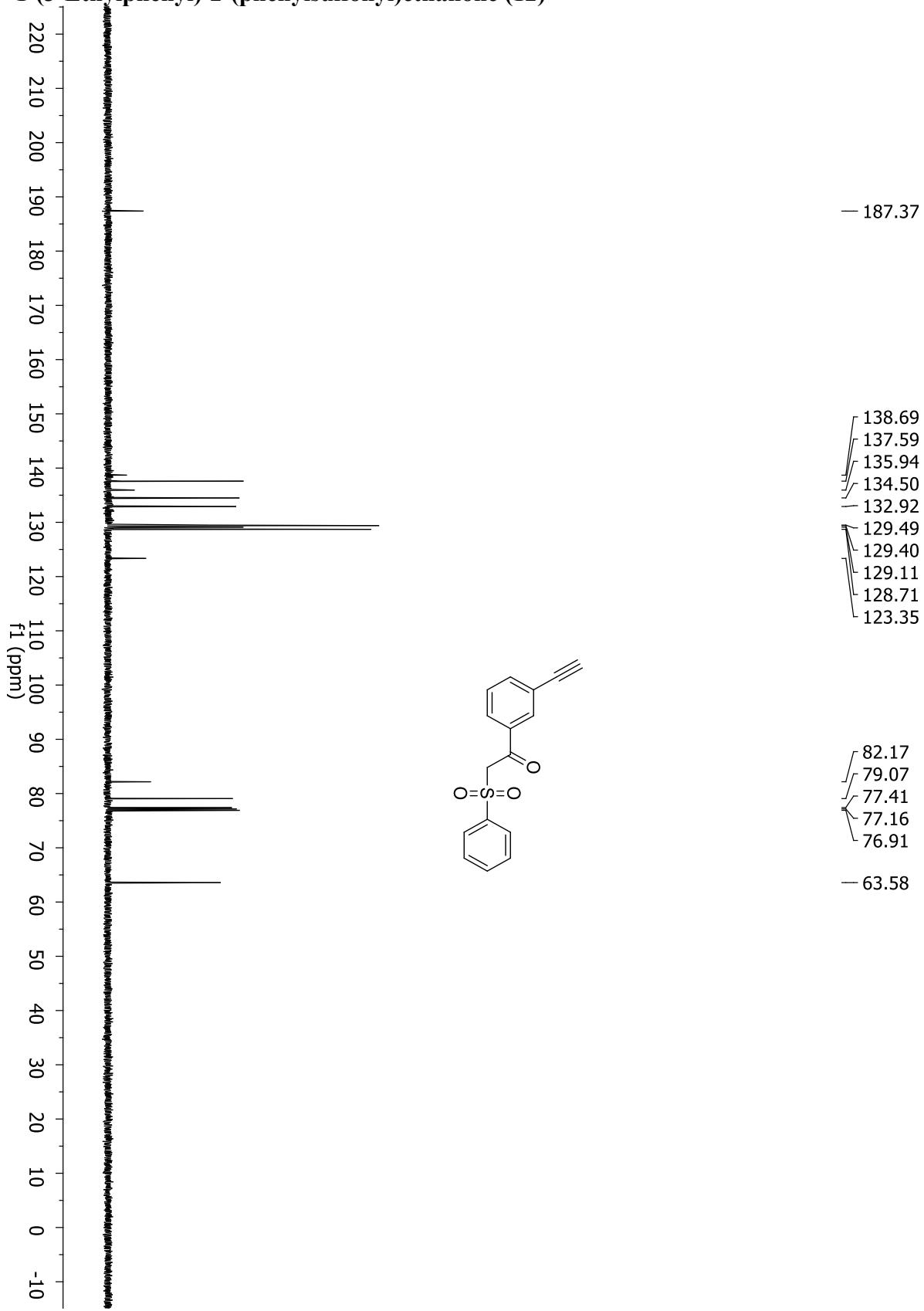
**1-(4-Acetylphenyl)-2-(phenylsulfonyl)ethanone (11)**



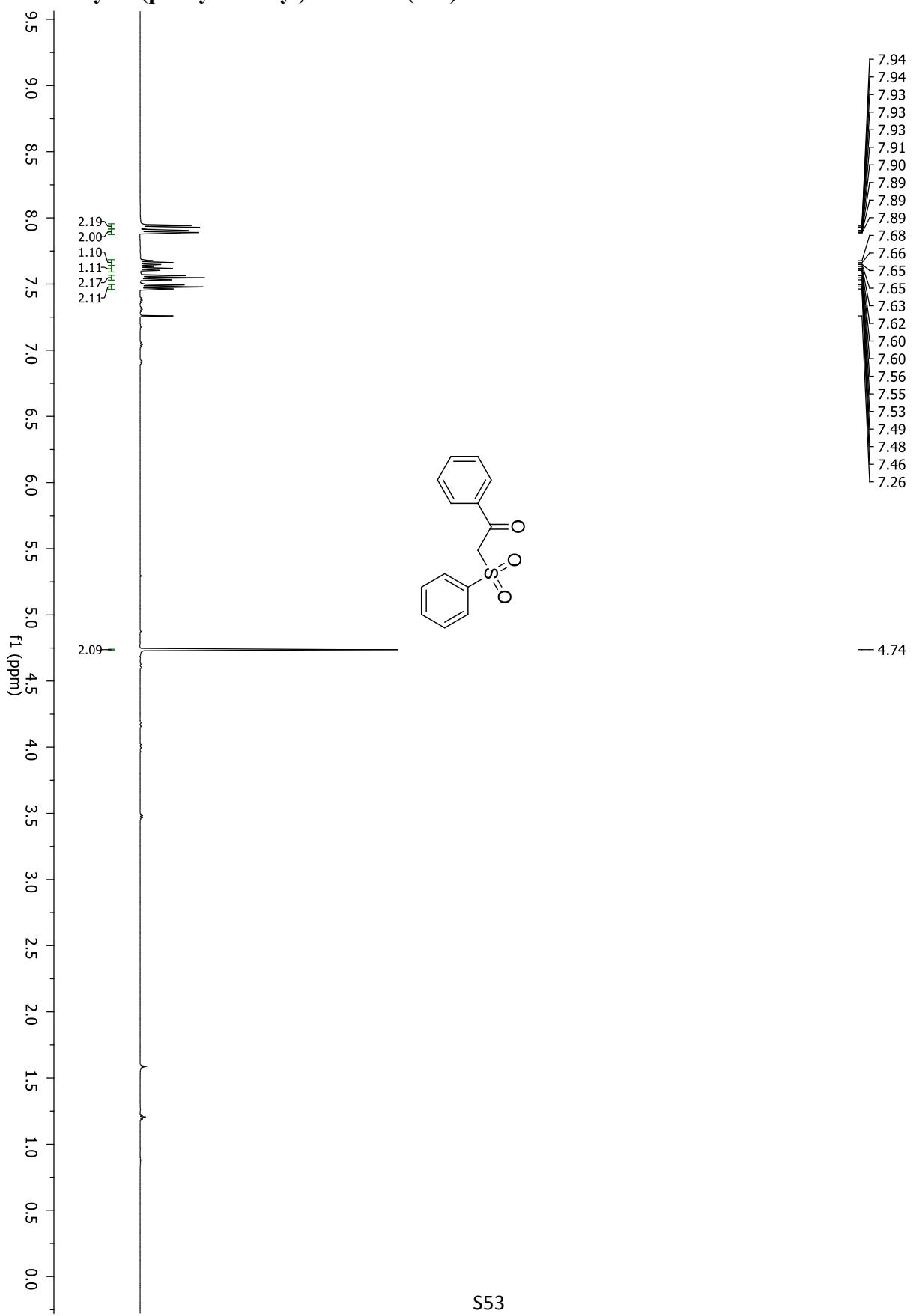
### **1-(3-Ethylphenyl)-2-(phenylsulfonyl)ethanone (12)**



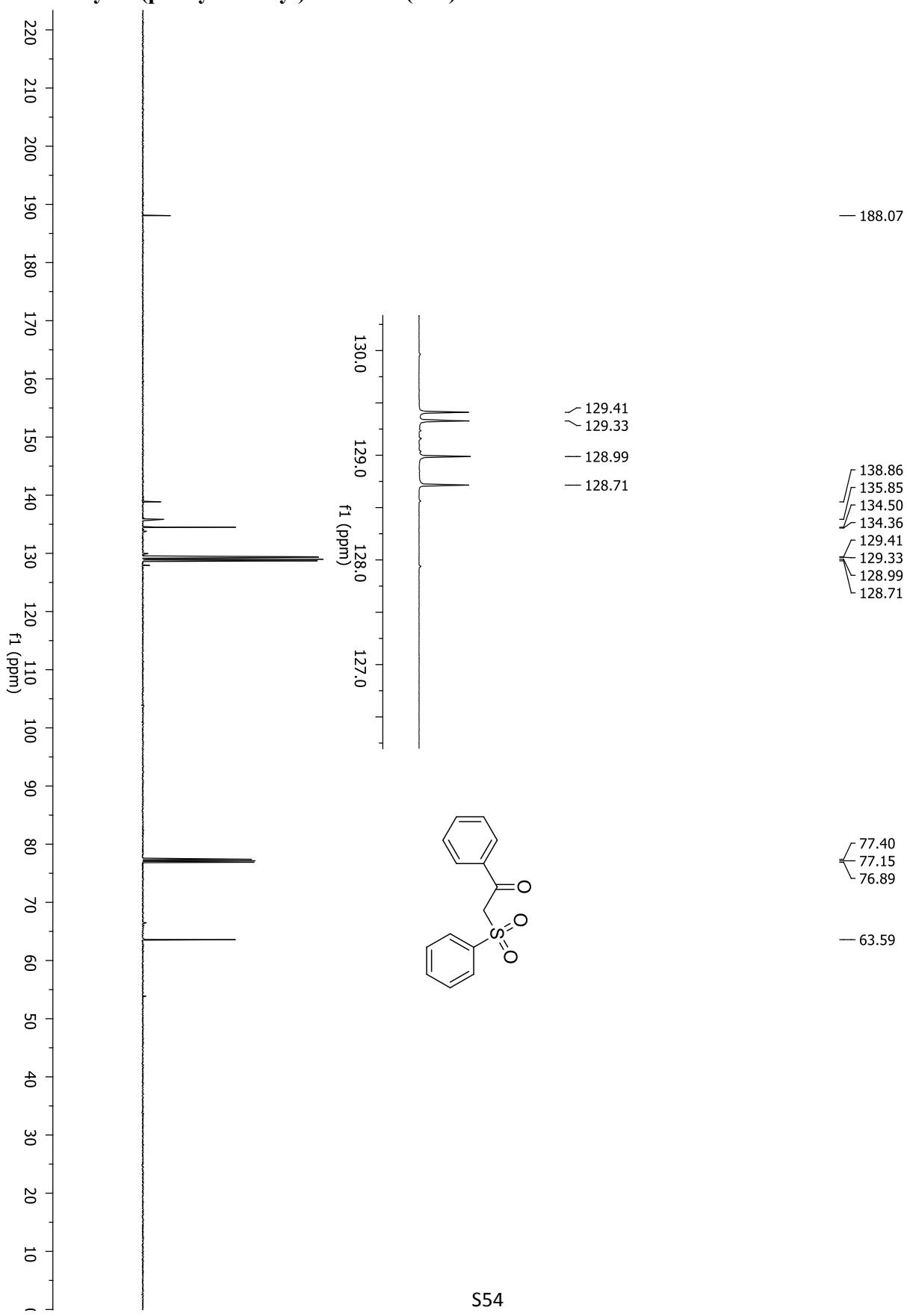
**1-(3-Ethylphenyl)-2-(phenylsulfonyl)ethanone (12)**



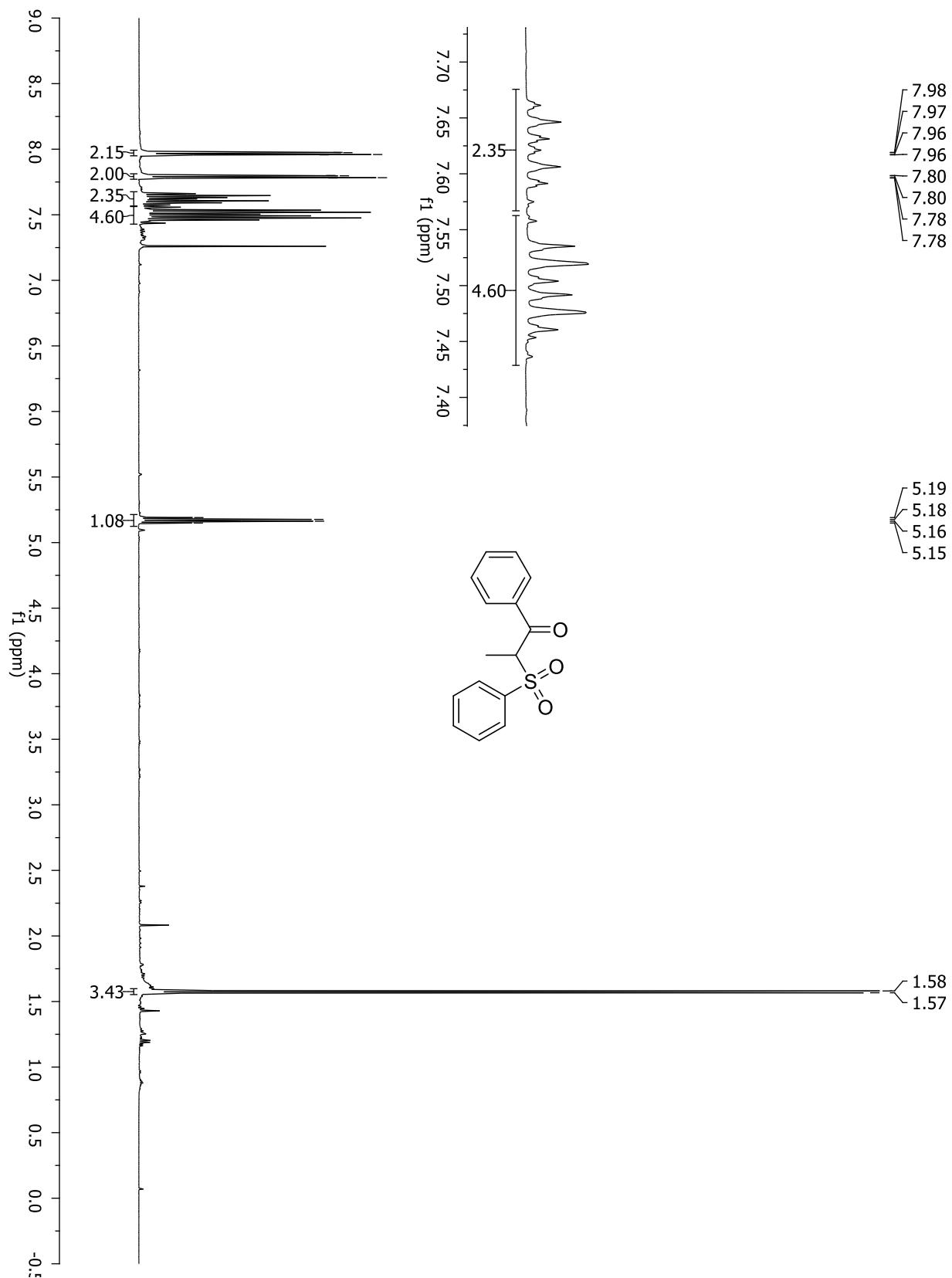
**1-Phenyl-2-(phenylsulfonyl)ethanone (13a)**



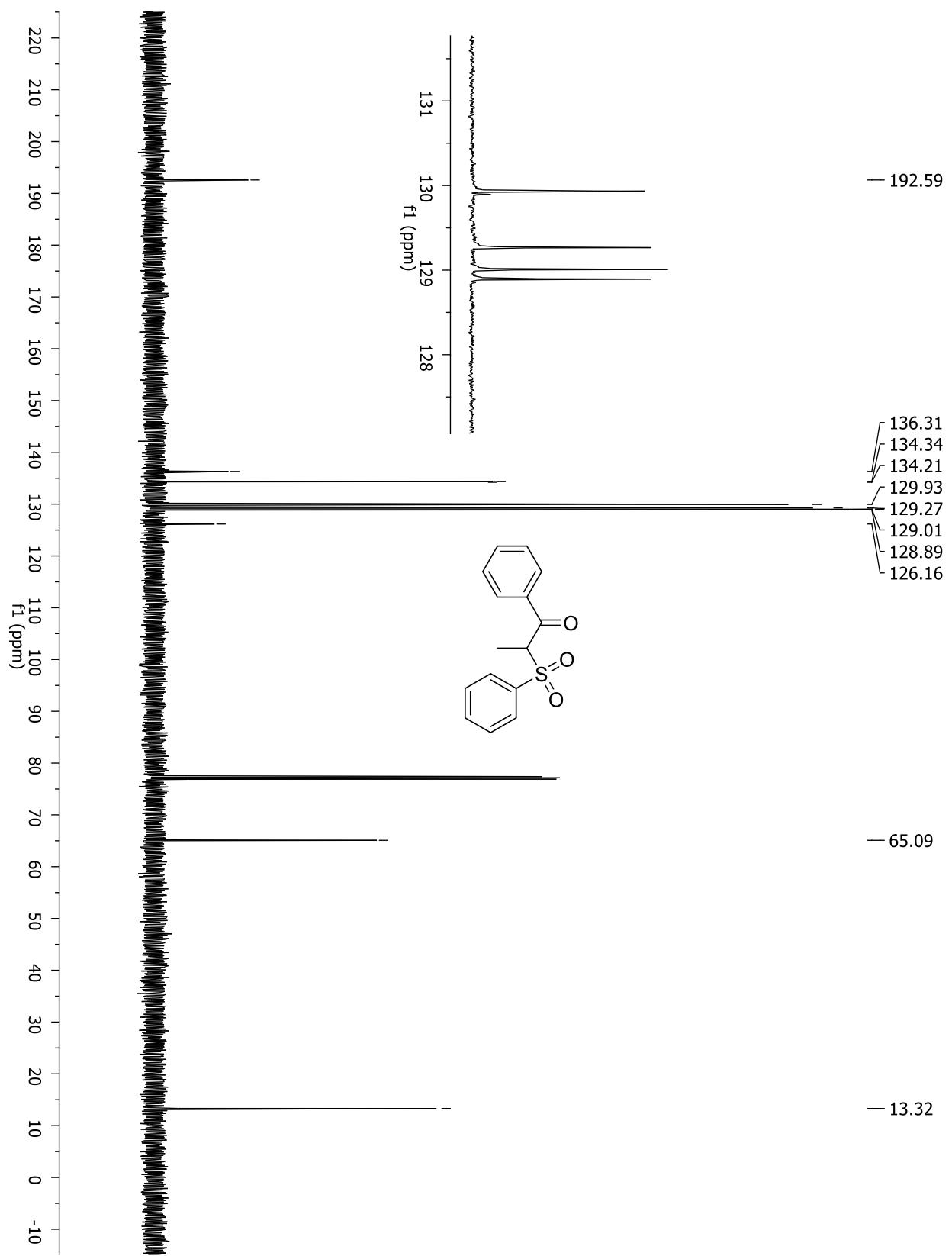
**1-Phenyl-2-(phenylsulfonyl)ethanone (13a)**



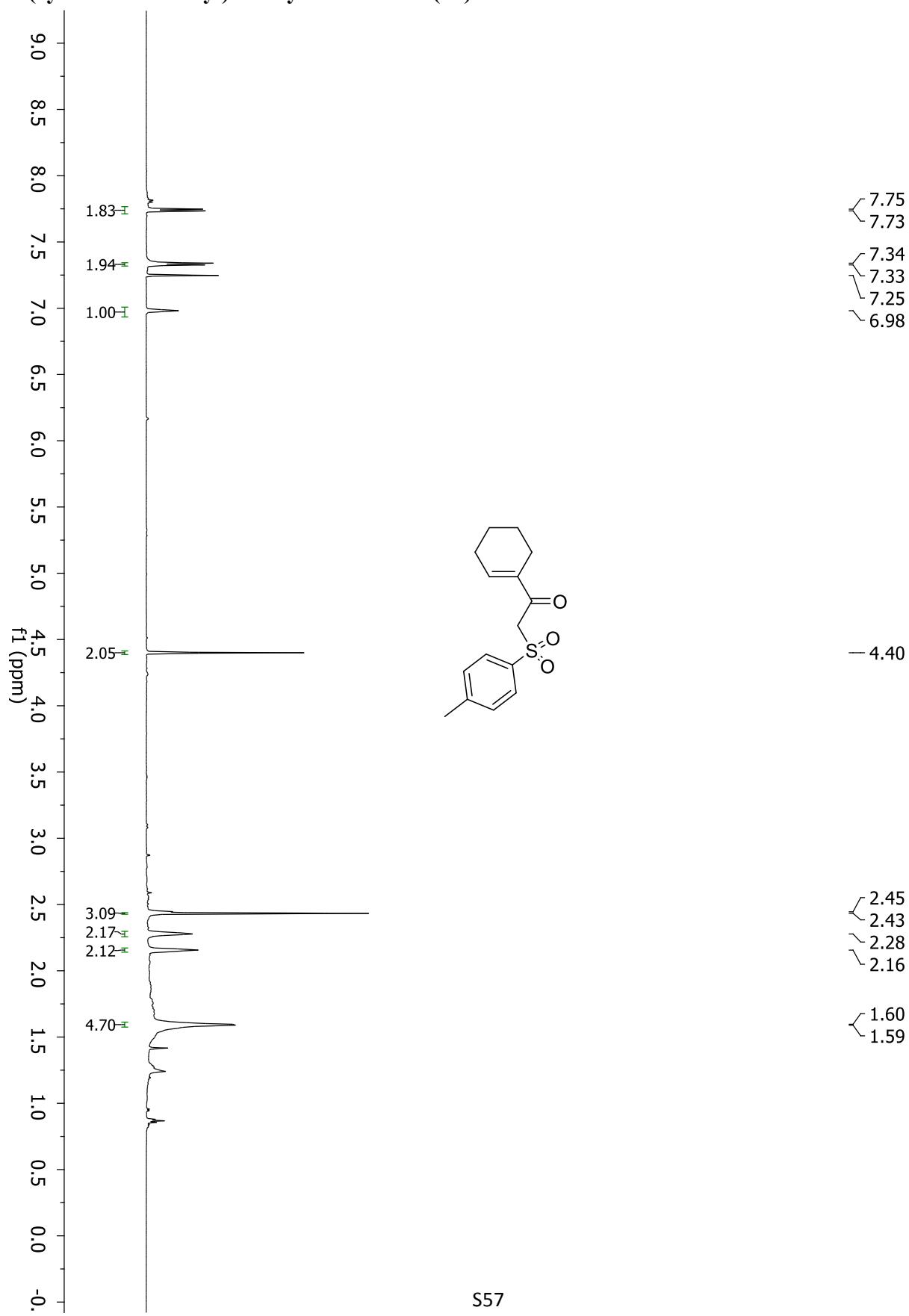
**1-Phenyl-2-(phenylsulfonyl)propan-1-one (13b)**



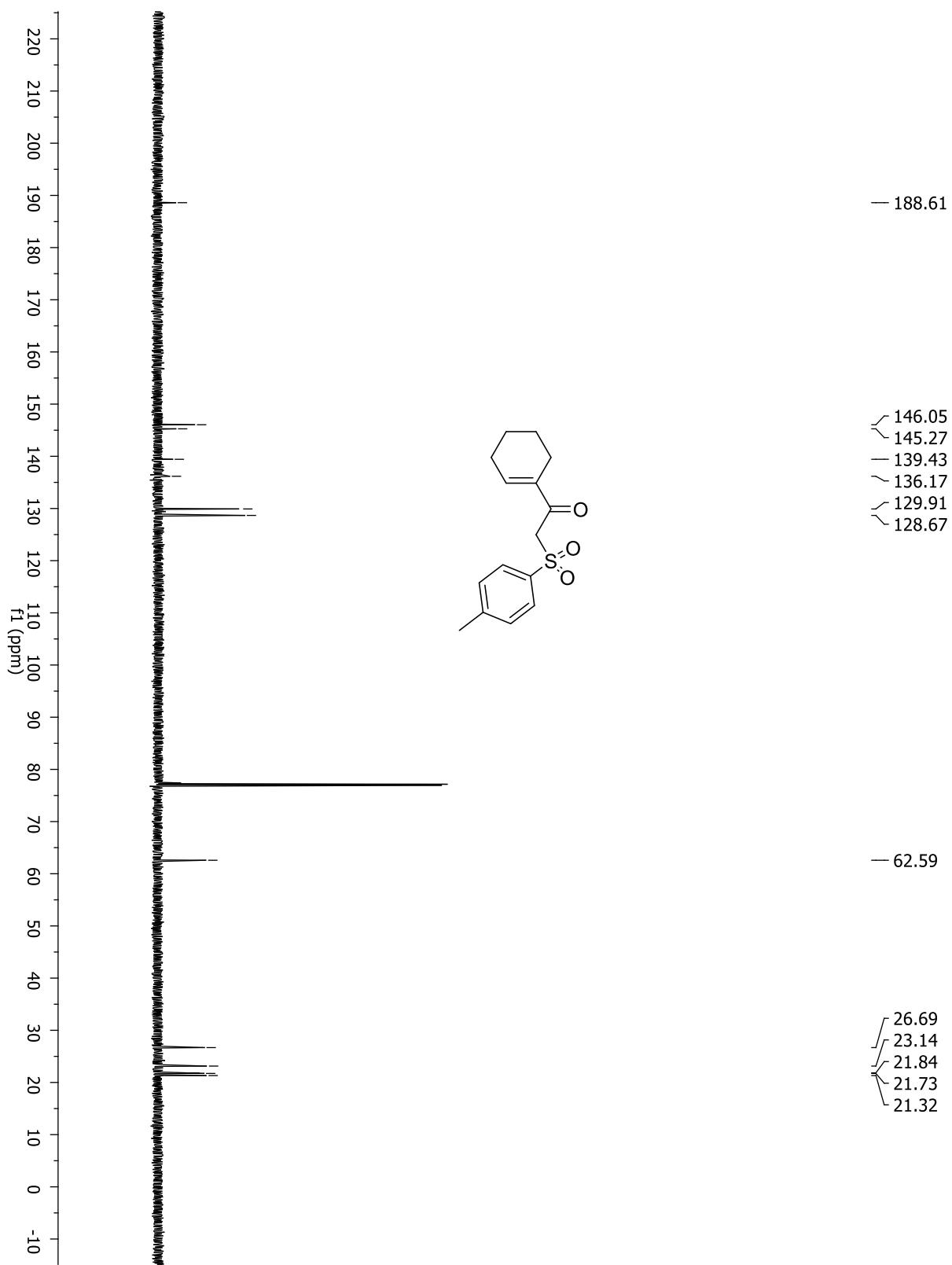
**1-Phenyl-2-(phenylsulfonyl)propan-1-one (13b)**



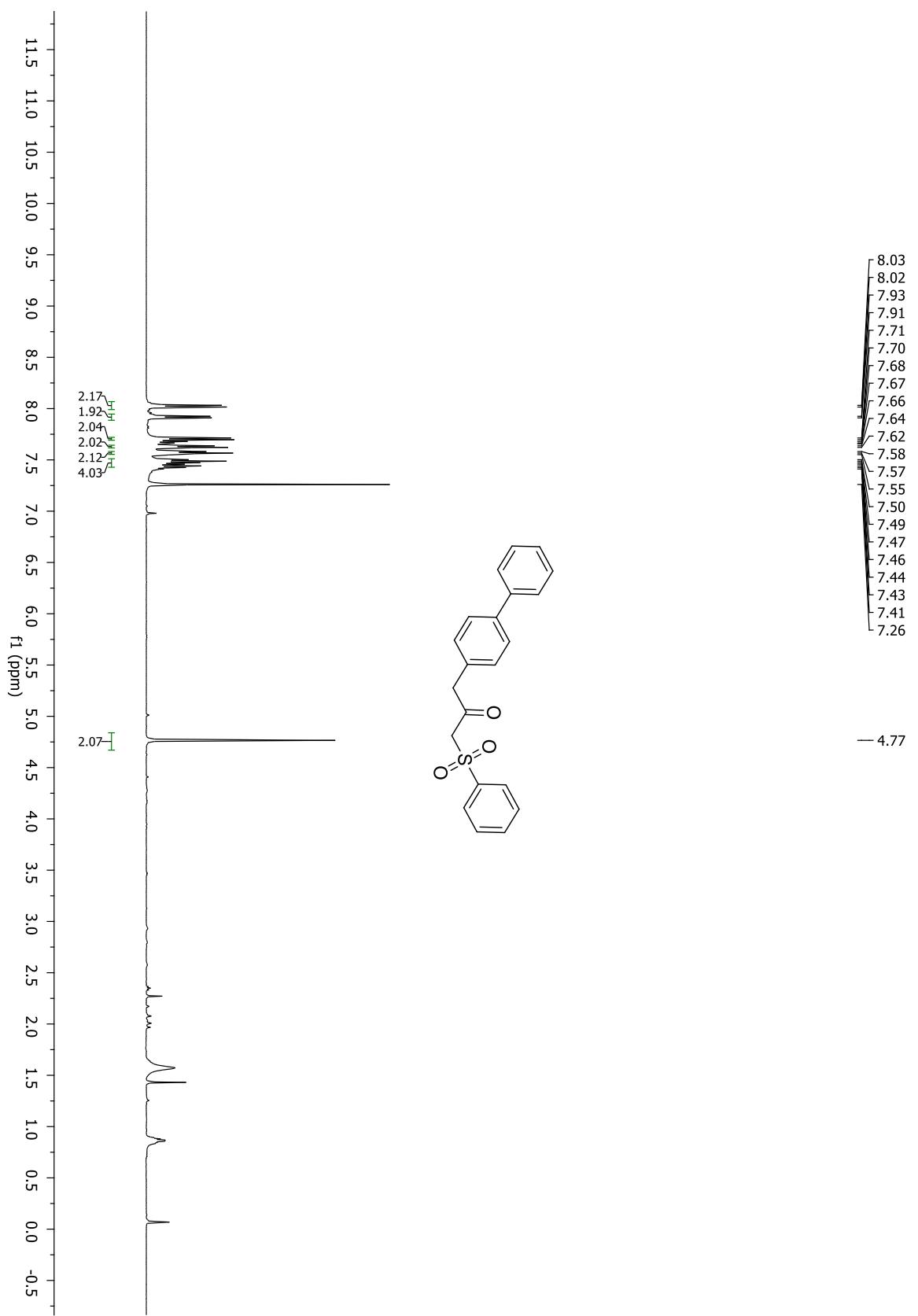
**1-(cyclohex-1-en-1-yl)-2-tosylethan-1-one (14)**



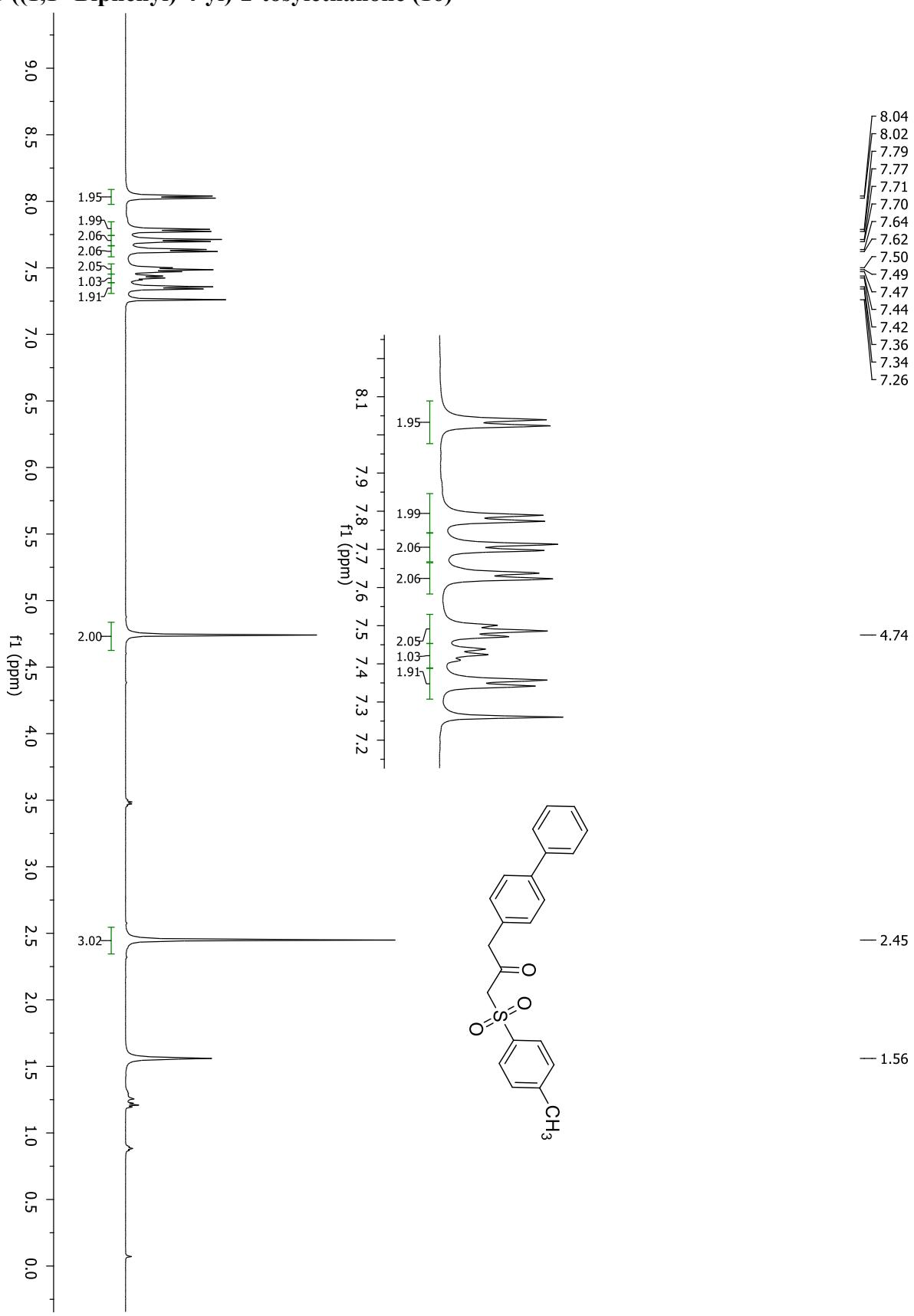
**1-(cyclohex-1-en-1-yl)-2-tosylethan-1-one (14)**



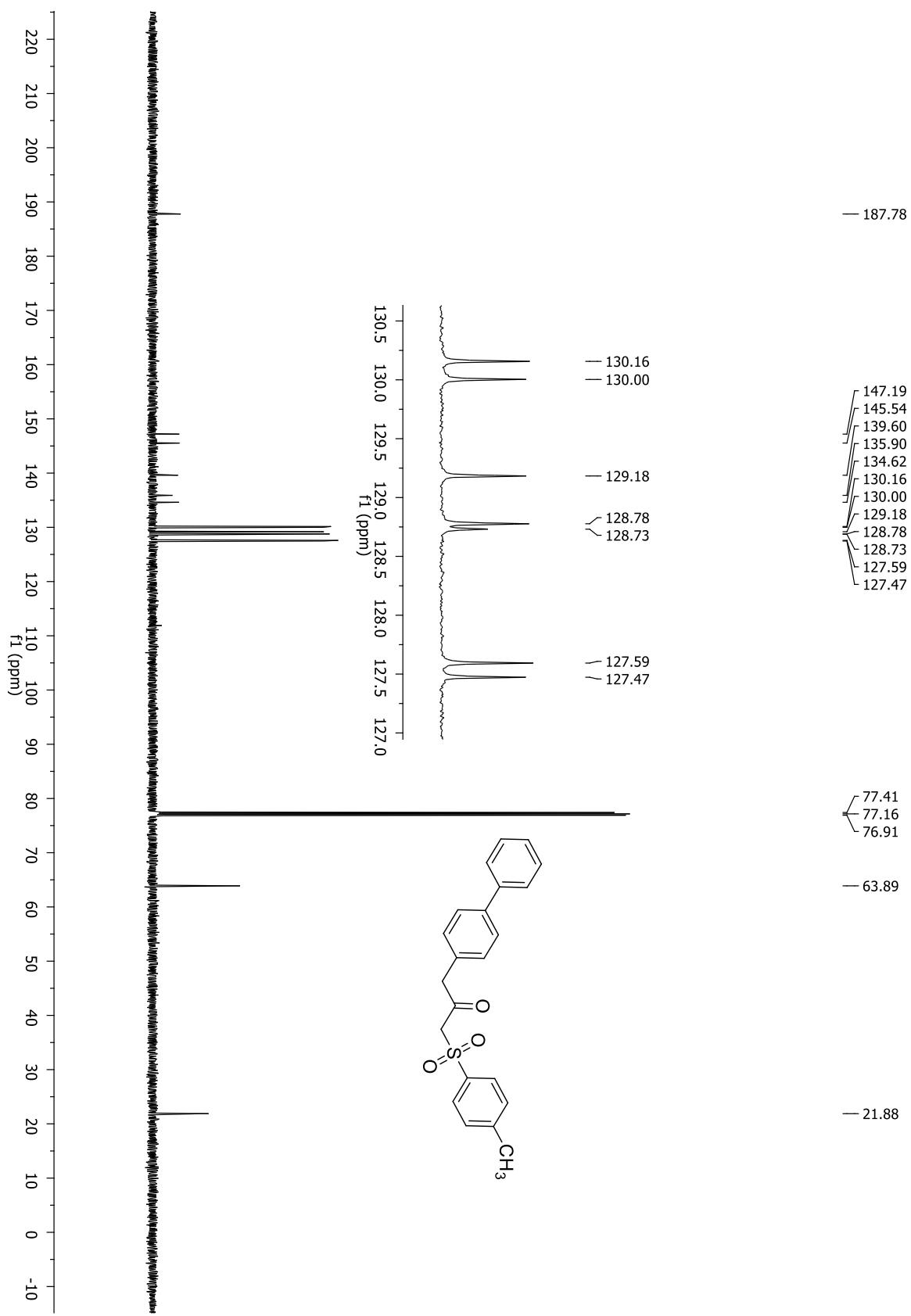
**1-([1,1'-Biphenyl]-4-yl)-2-(phenylsulfonyl)ethanone (15)**



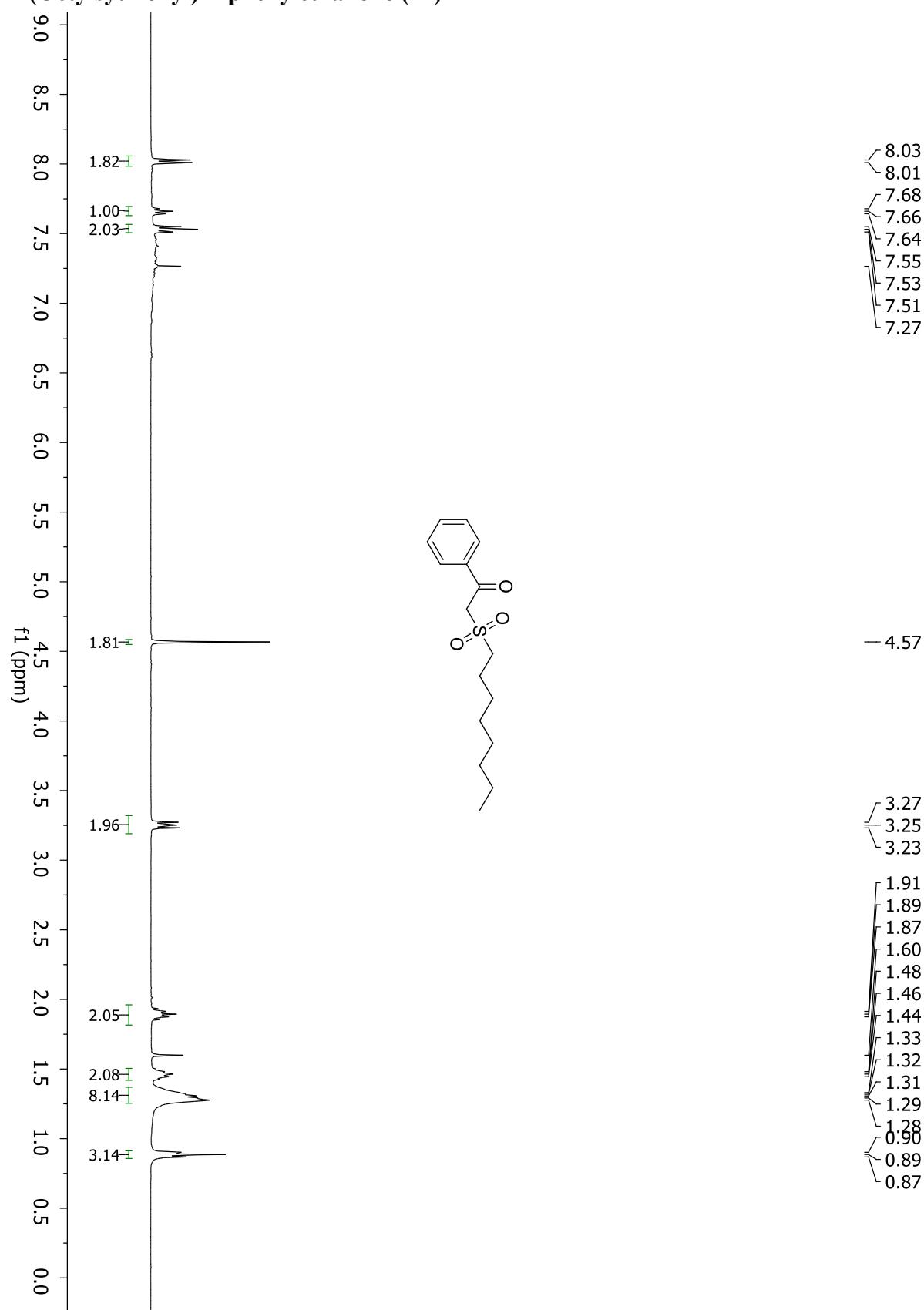
**1-((1,1'-Biphenyl)-4-yl)-2-tosylethanone (16)**



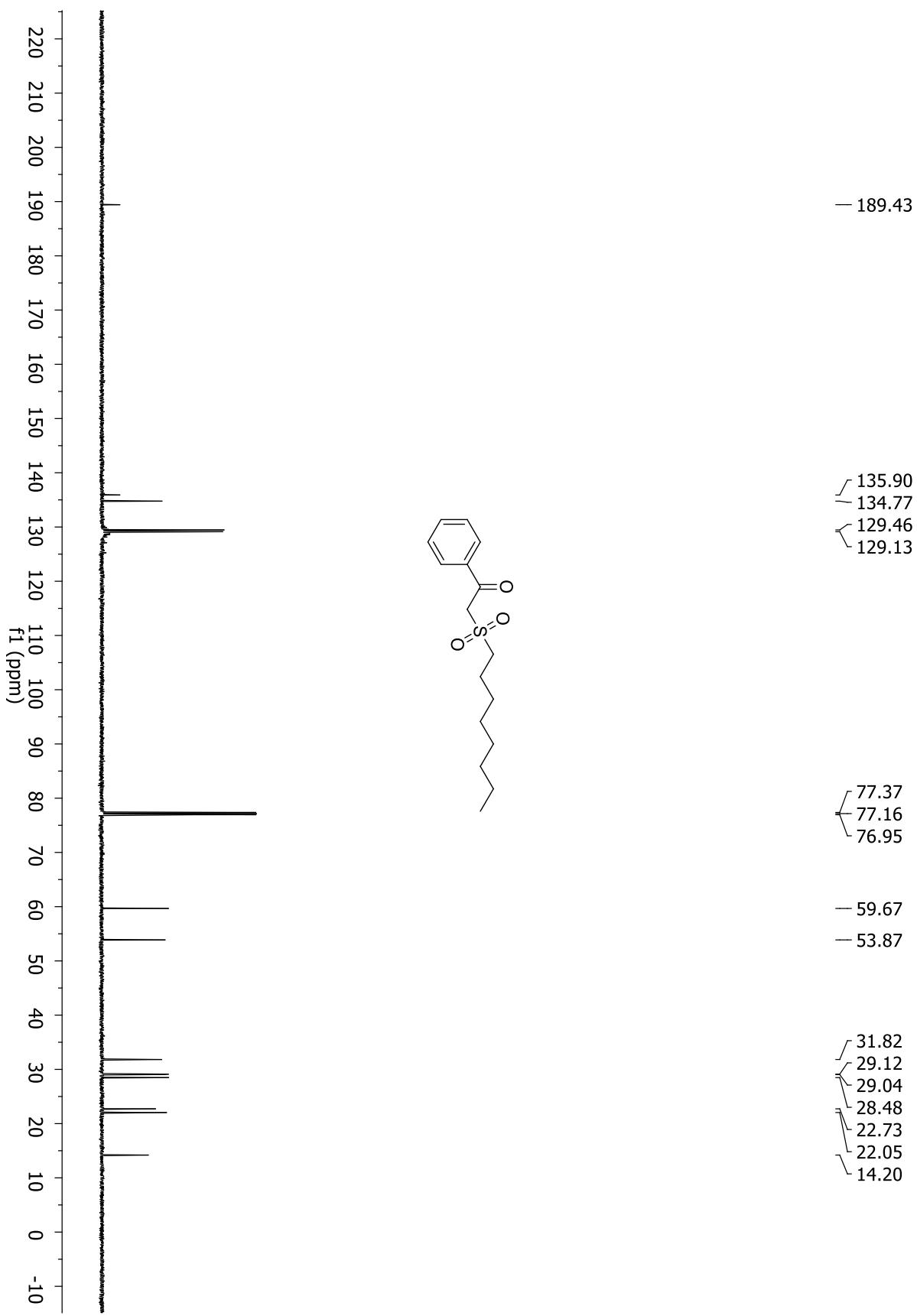
**1-((1,1'-Biphenyl)-4-yl)-2-tosylethanone (16)**



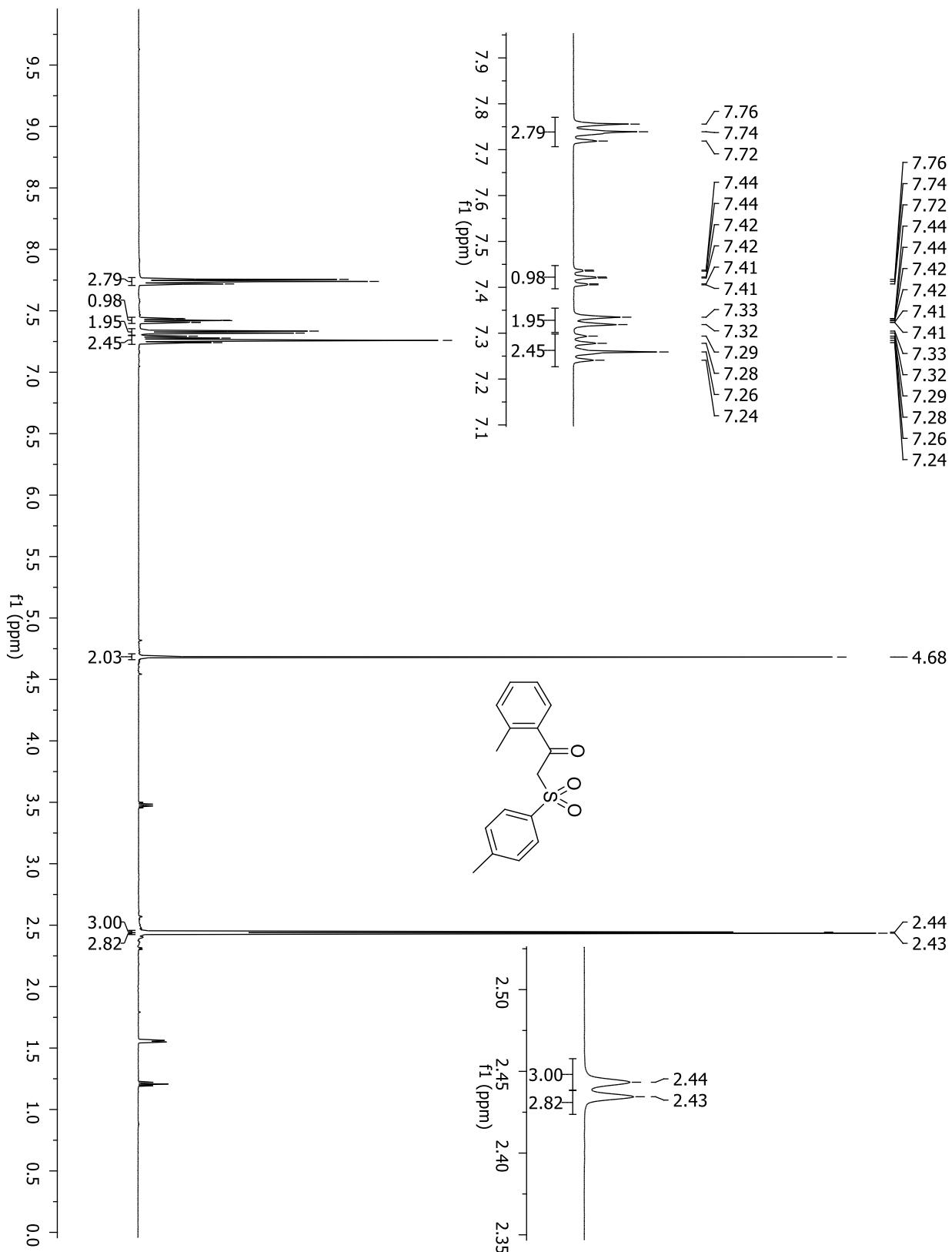
**2-(Octylsulfonyl)-1-phenylethanone (17)**



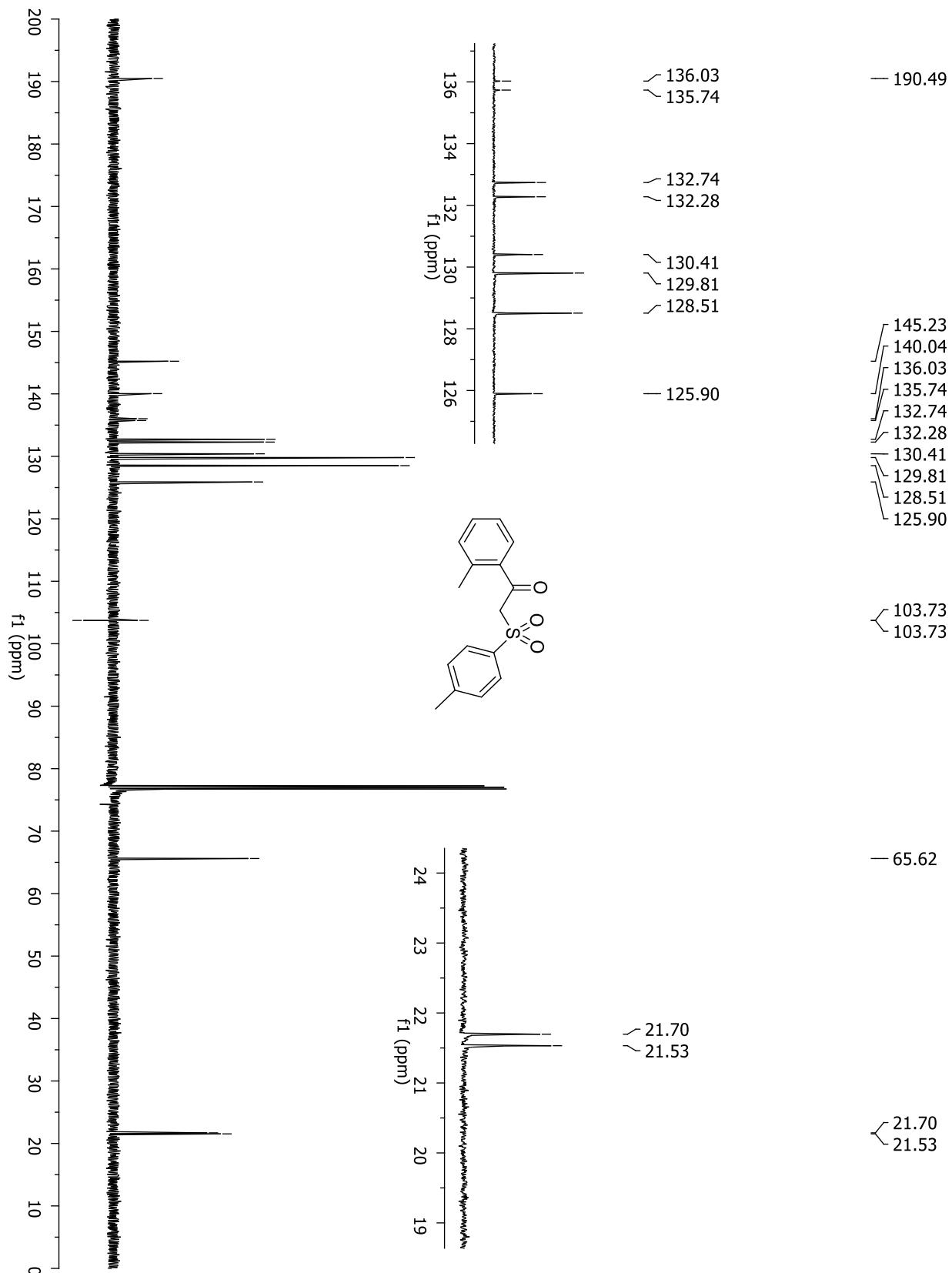
**2-(Octylsulfonyl)-1-phenylethanone (17)**



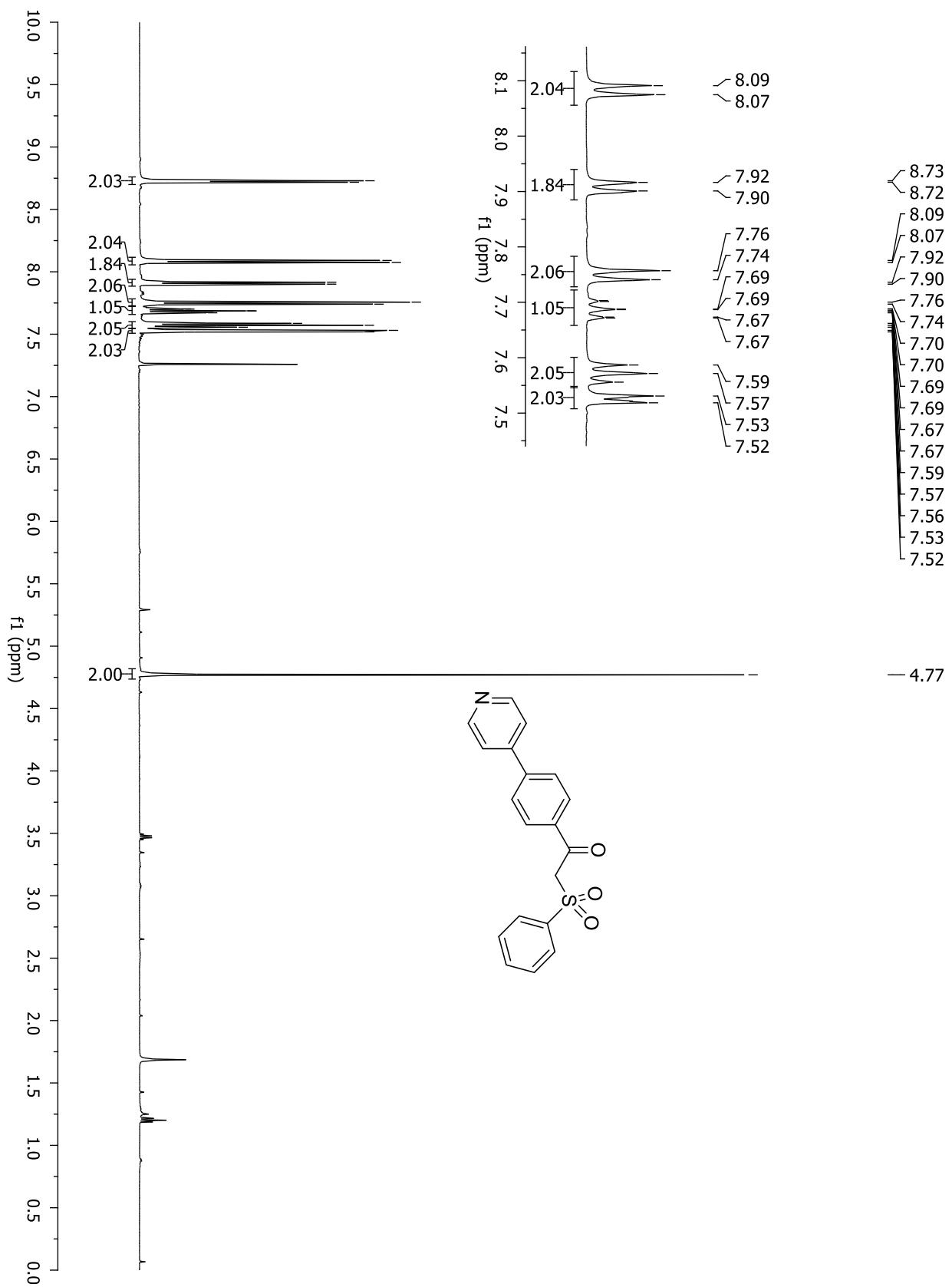
**1-(o-tolyl)-2-tosylethan-1-one (18)**



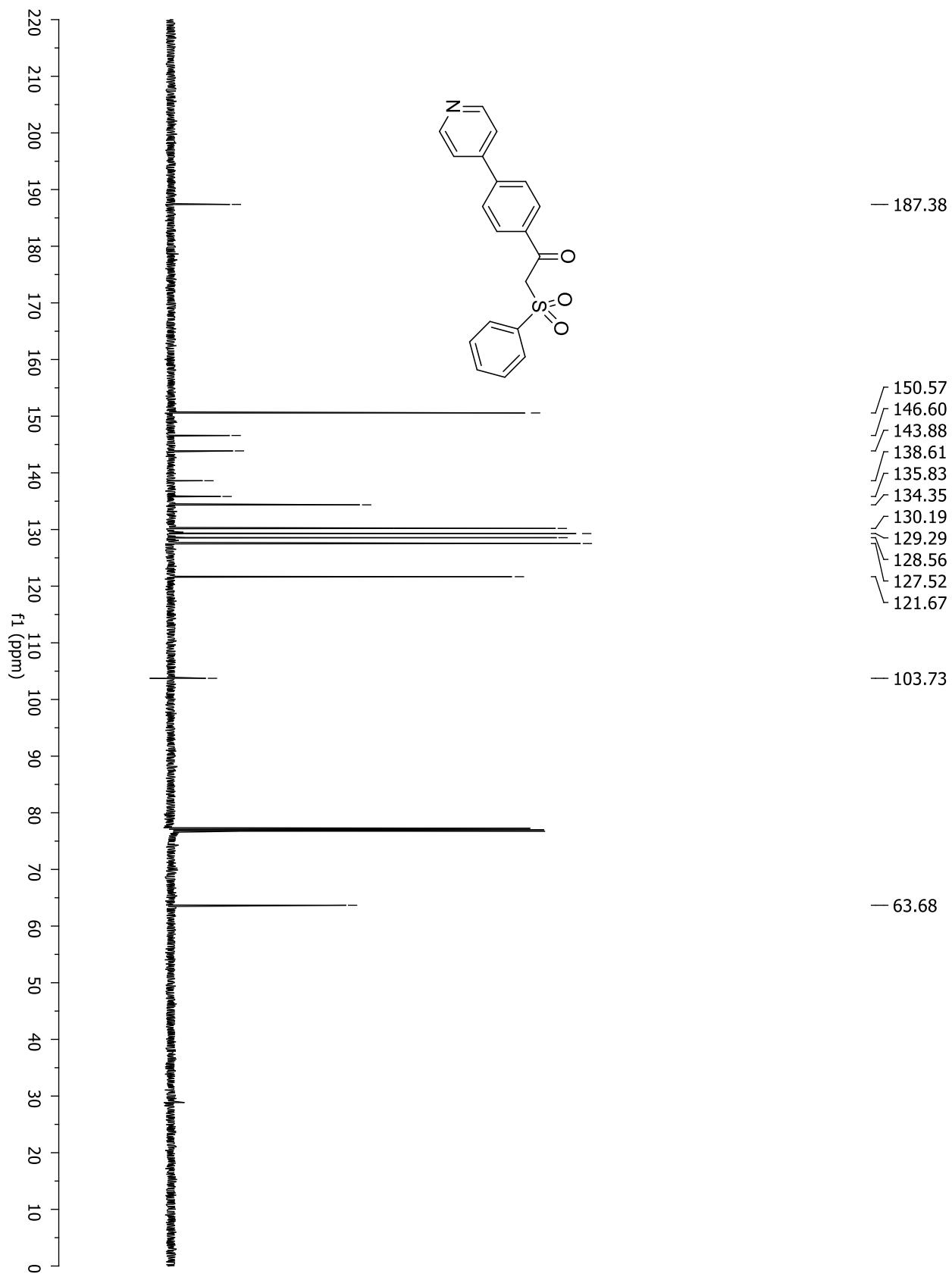
**1-(o-tolyl)-2-tosylethan-1-one (18)**



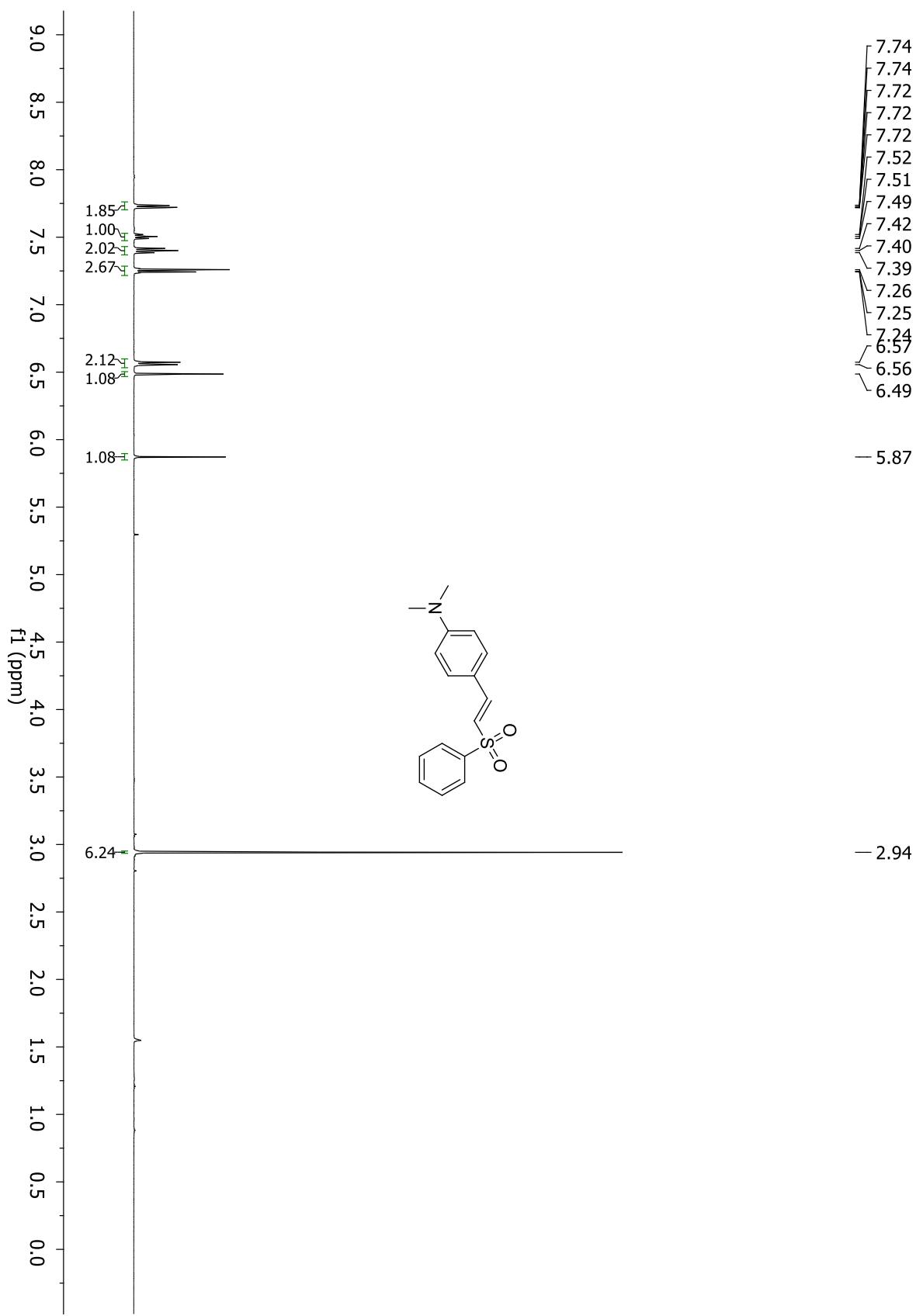
**2-(phenylsulfonyl)-1-(4-(pyridin-4-yl)phenyl)ethan-1-one (20)**



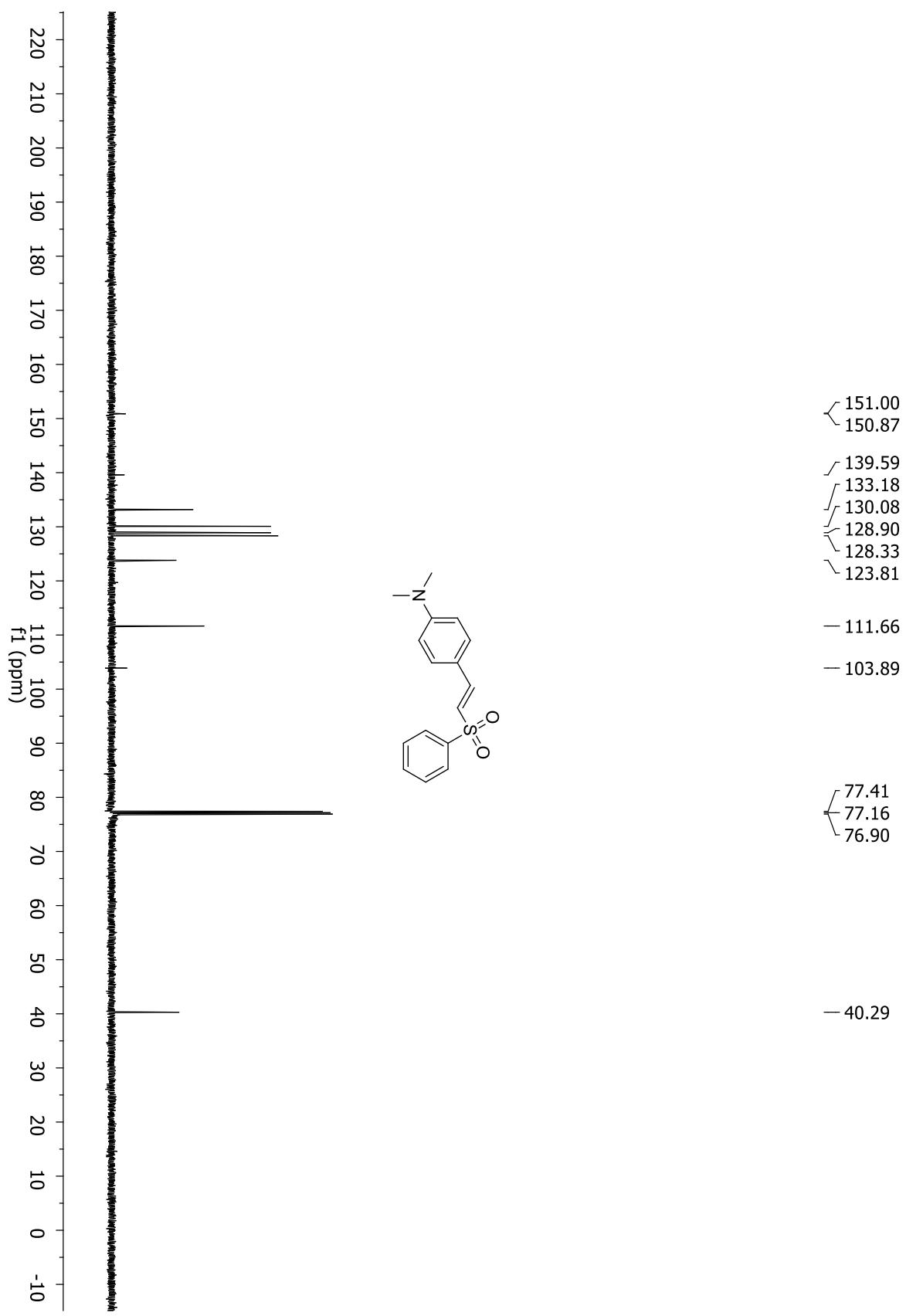
**2-(phenylsulfonyl)-1-(4-(pyridin-4-yl)phenyl)ethan-1-one (20)**



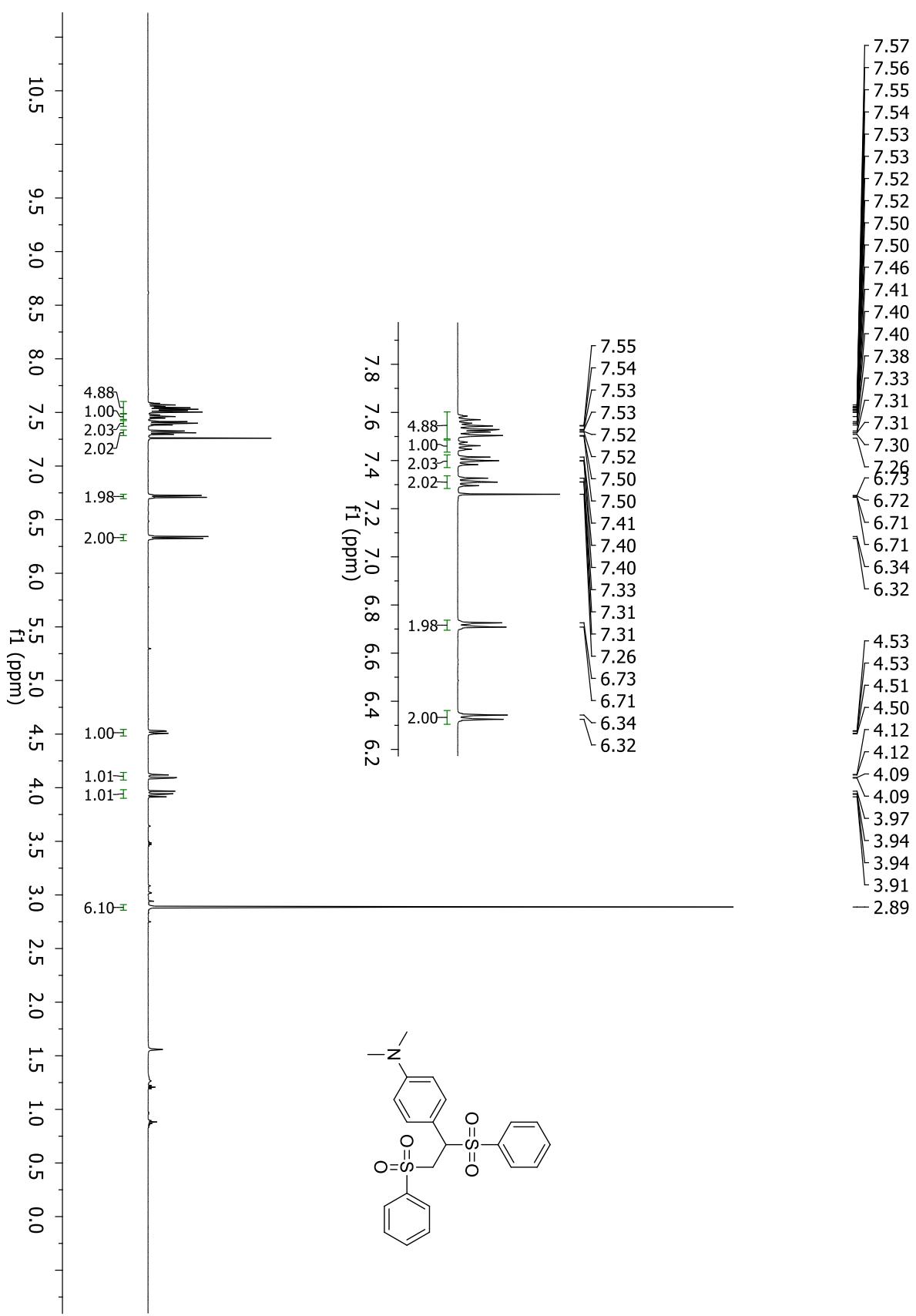
**(E)-N,N-Dimethyl-4-(2-(phenylsulfonyl)vinyl)aniline (22)**



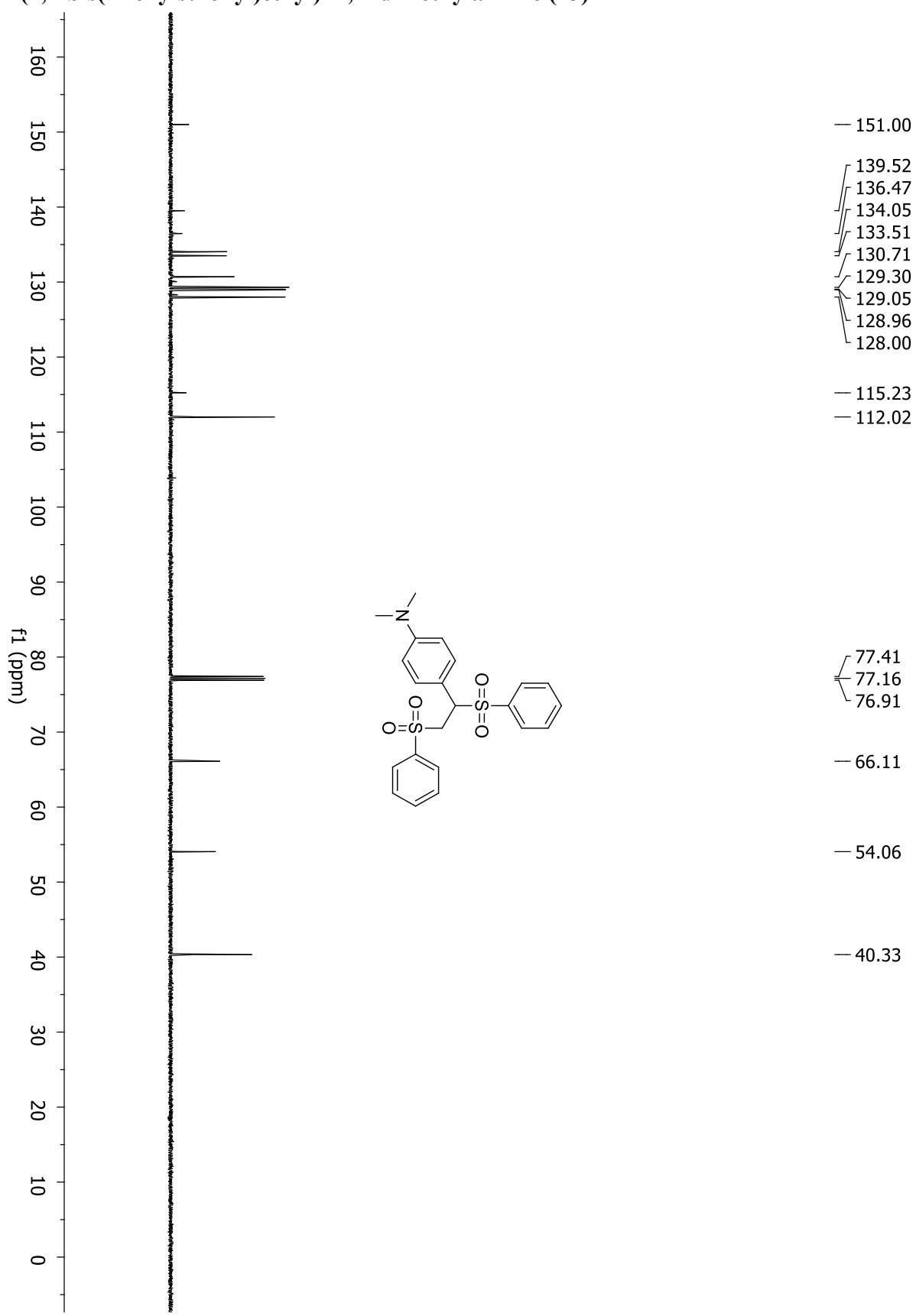
*(E)-N,N-Dimethyl-4-(2-(phenylsulfonyl)vinyl)aniline (22)*



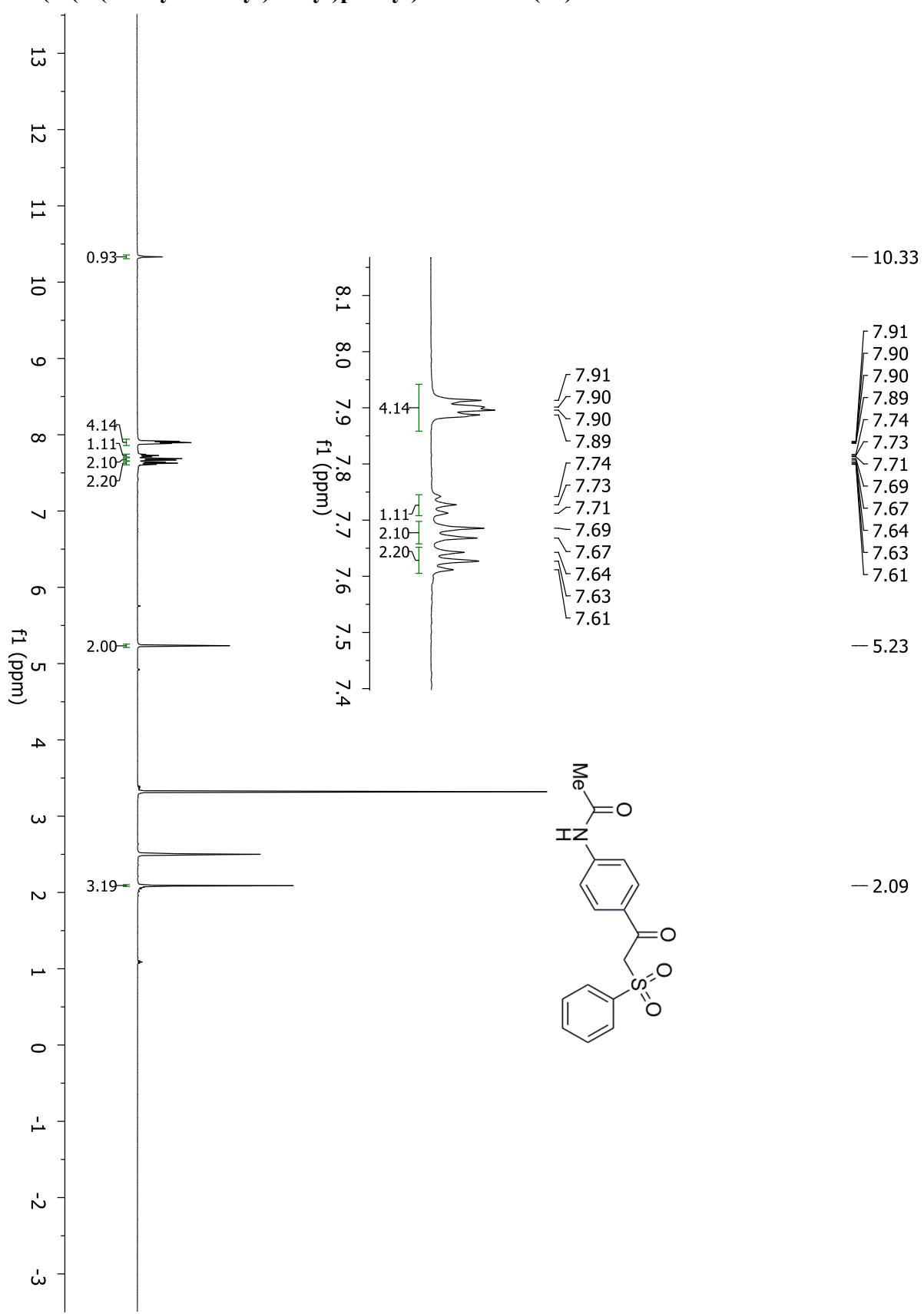
**4-(1,2-bis(Phenylsulfonyl)ethyl)-N,N-dimethylaniline (23)**



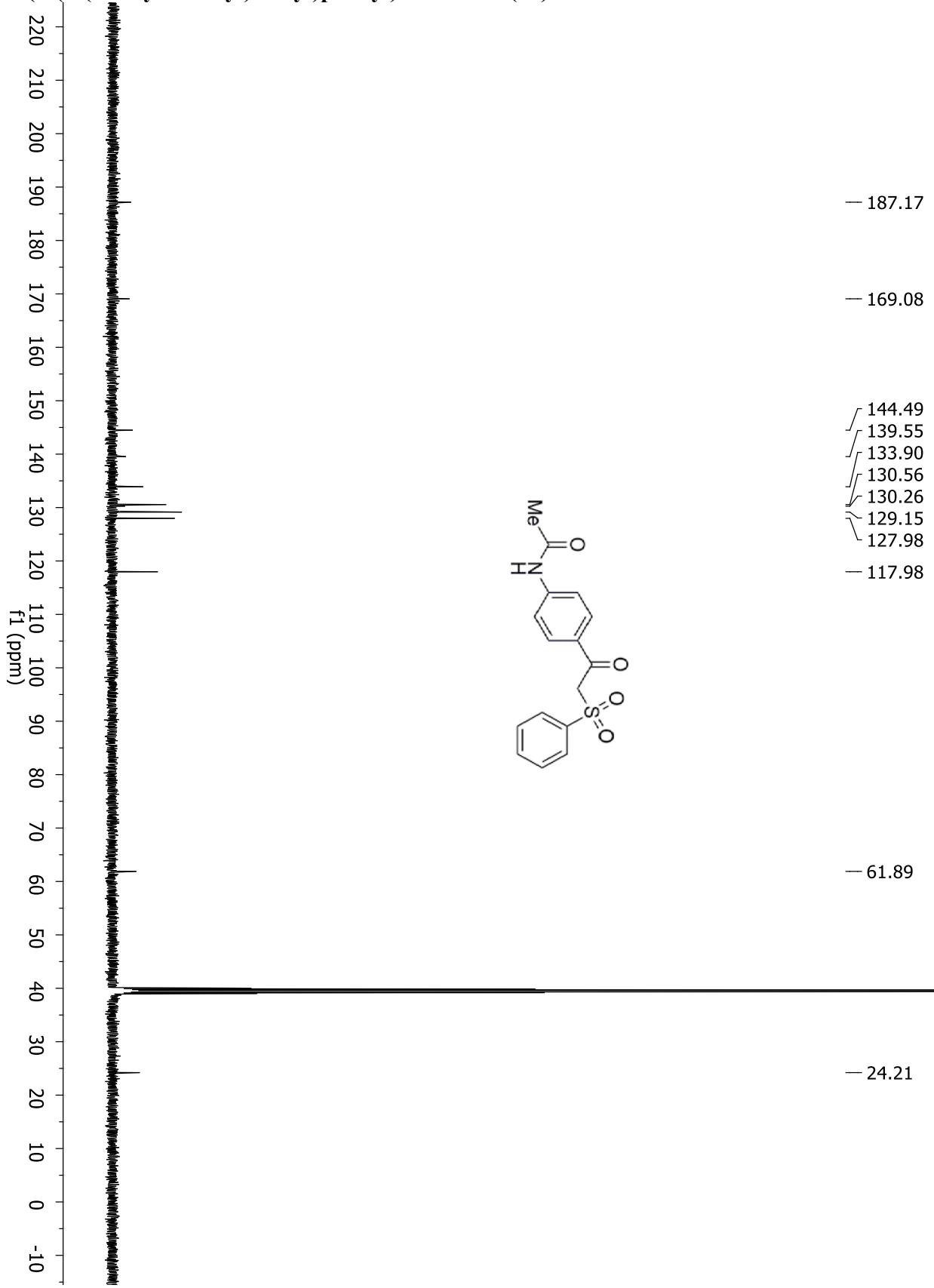
**4-(1,2-bis(Phenylsulfonyl)ethyl)-N,N-dimethylaniline (23)**



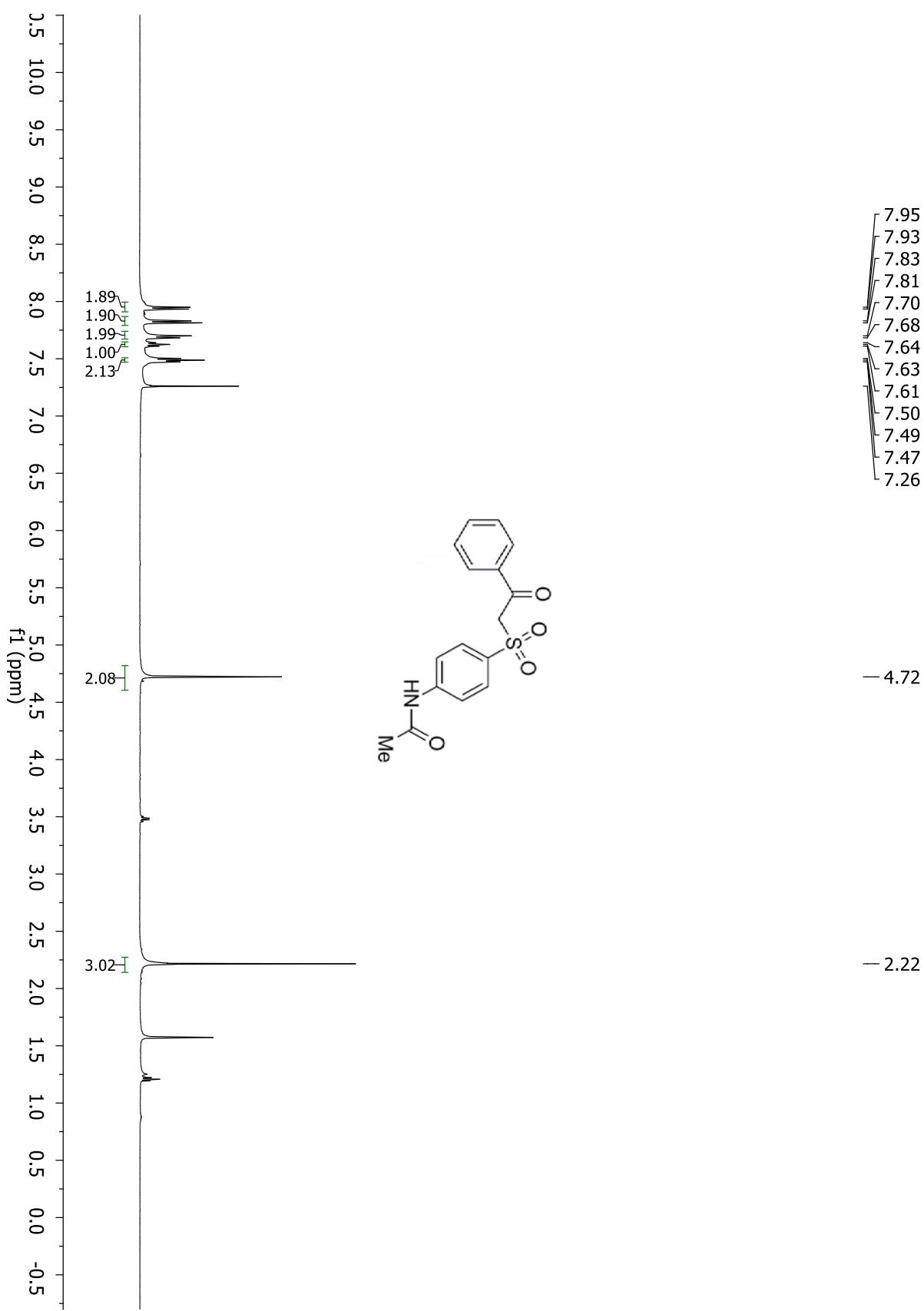
**N-(4-(2-(Phenylsulfonyl)acetyl)phenyl)acetamide (25)**



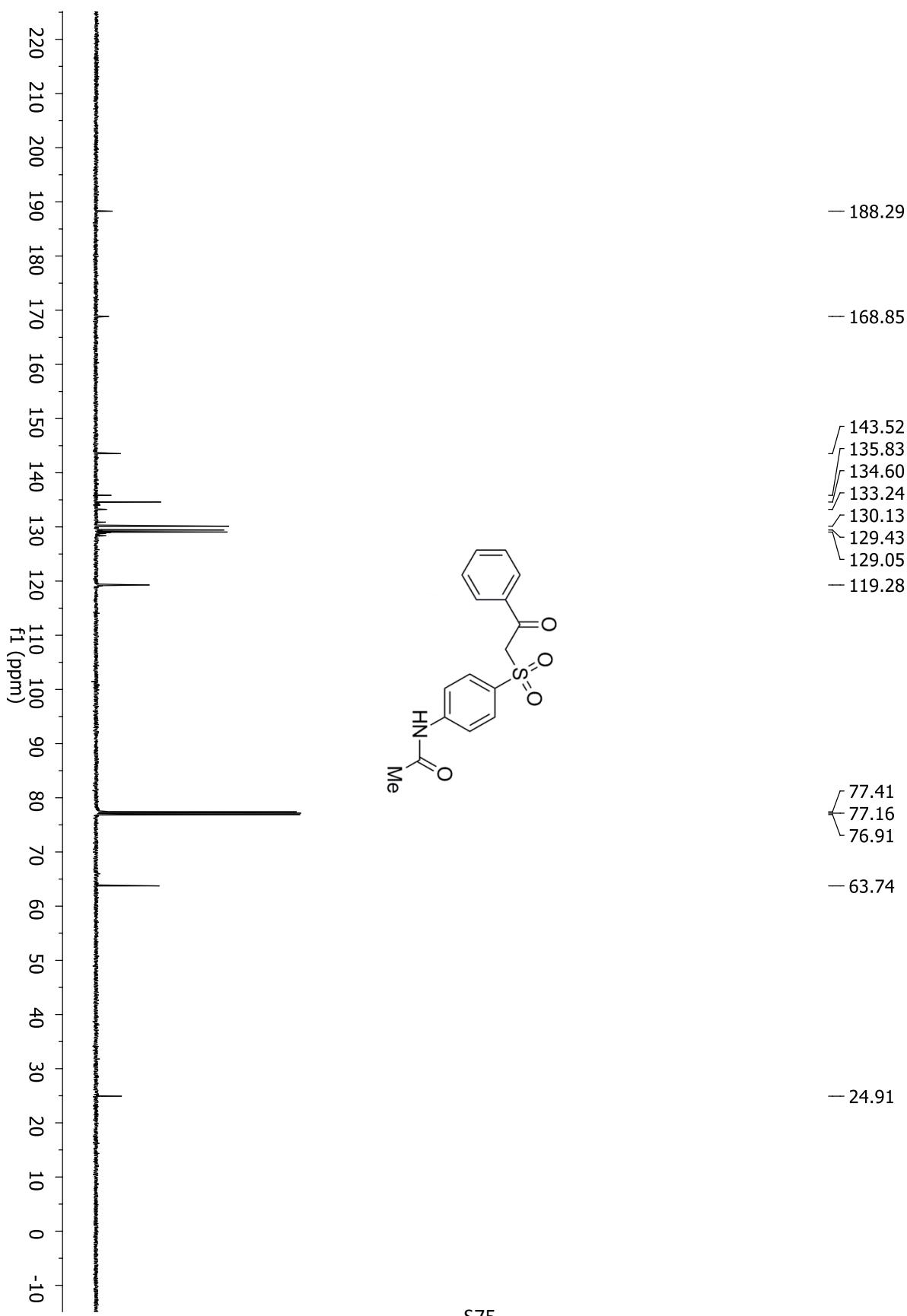
*N*-(4-(2-(Phenylsulfonyl)acetyl)phenyl)acetamide (25)



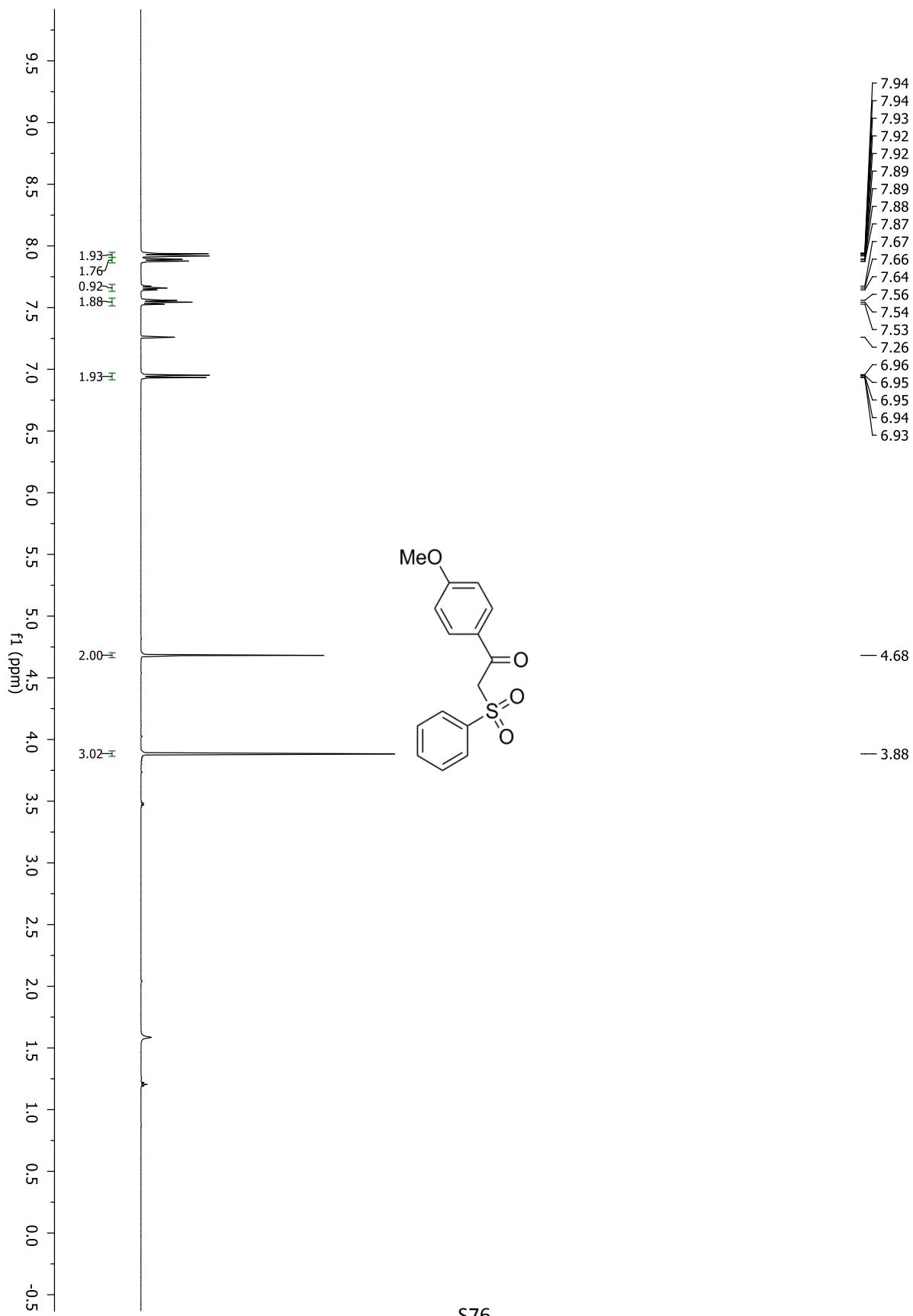
*N*-(4-((2-Oxo-2-phenylethyl)sulfonyl)phenyl)acetamide (26)



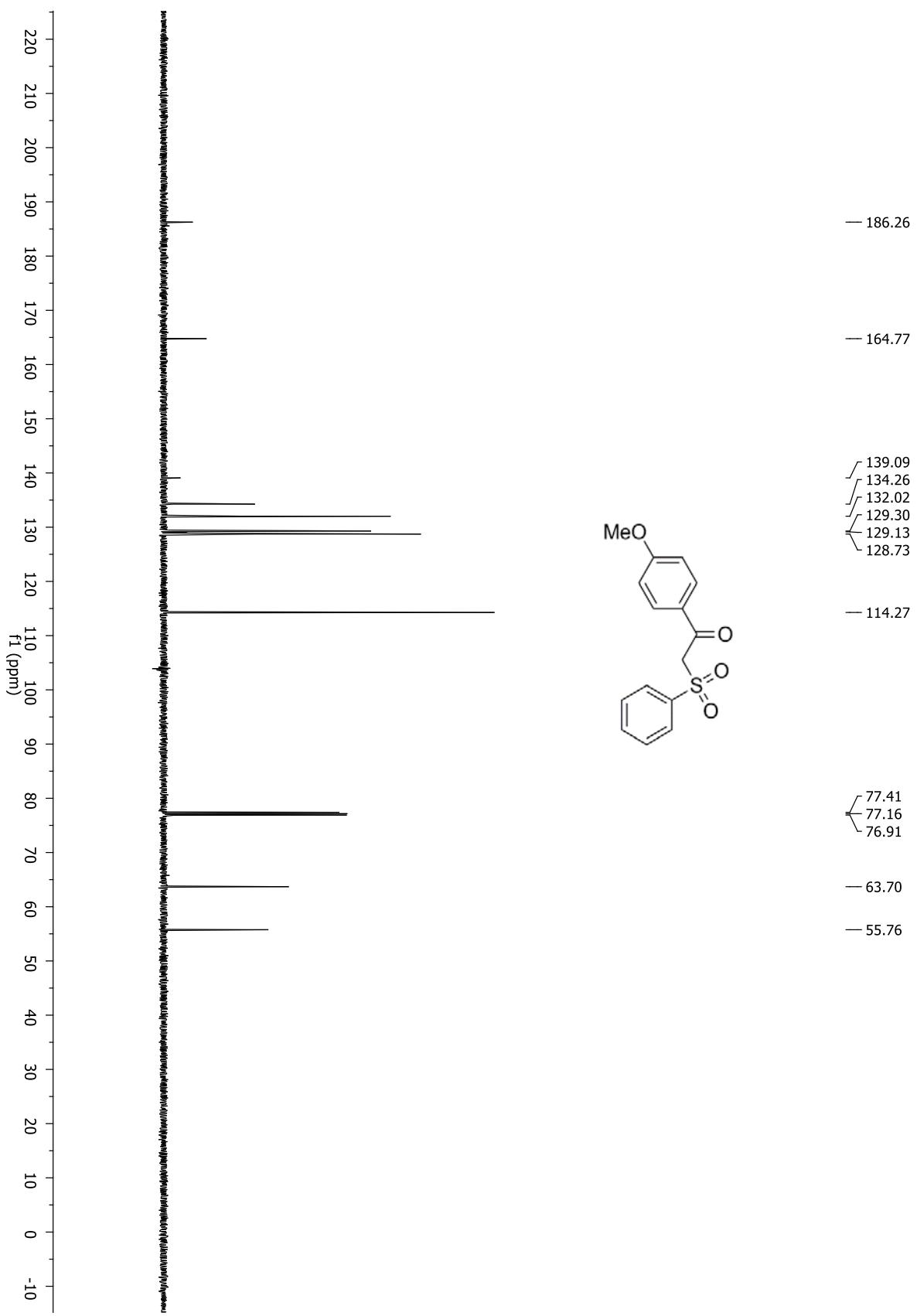
*N*-(4-((2-Oxo-2-phenylethyl)sulfonyl)phenyl)acetamide (26)



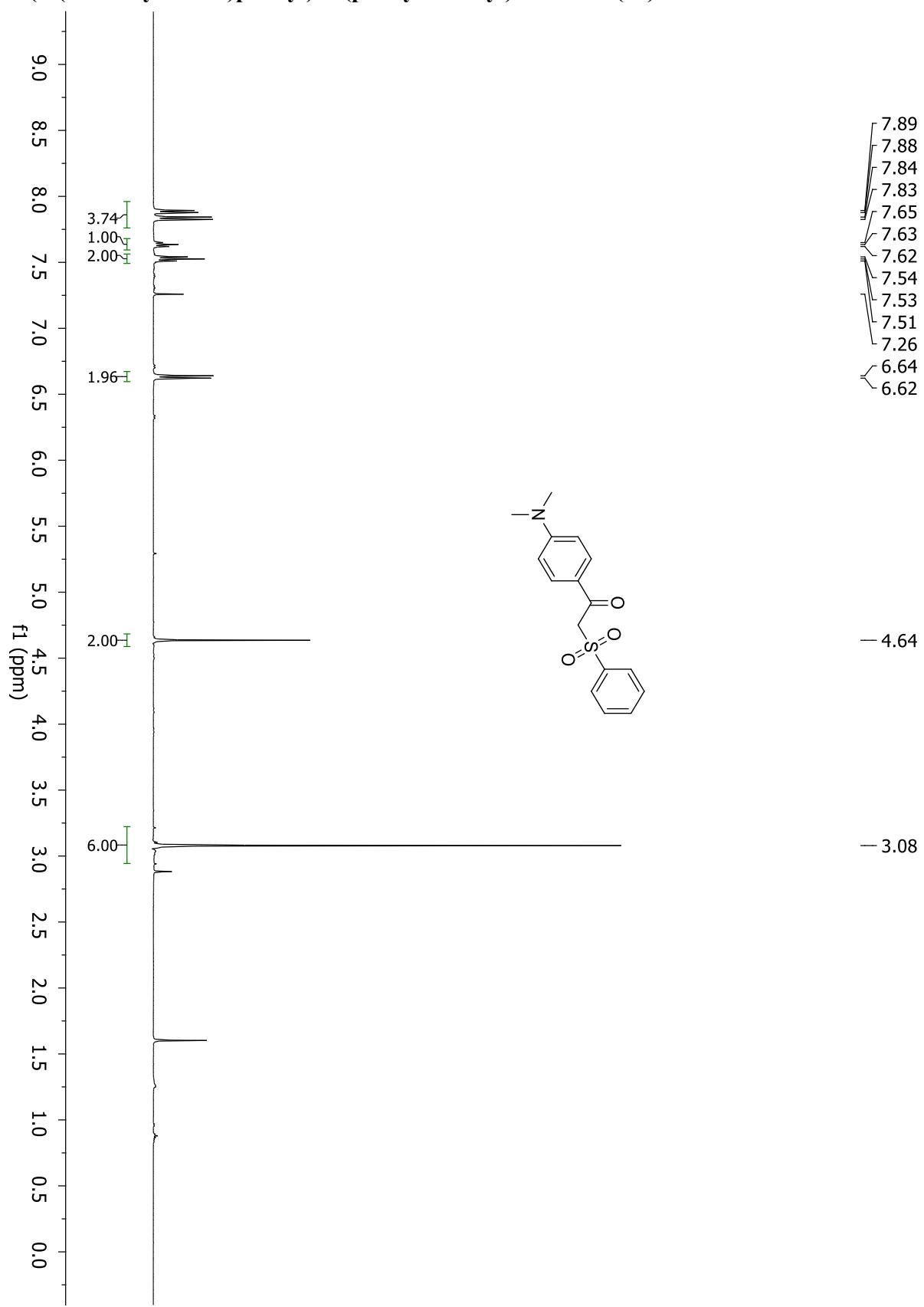
**1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethanone (28)**



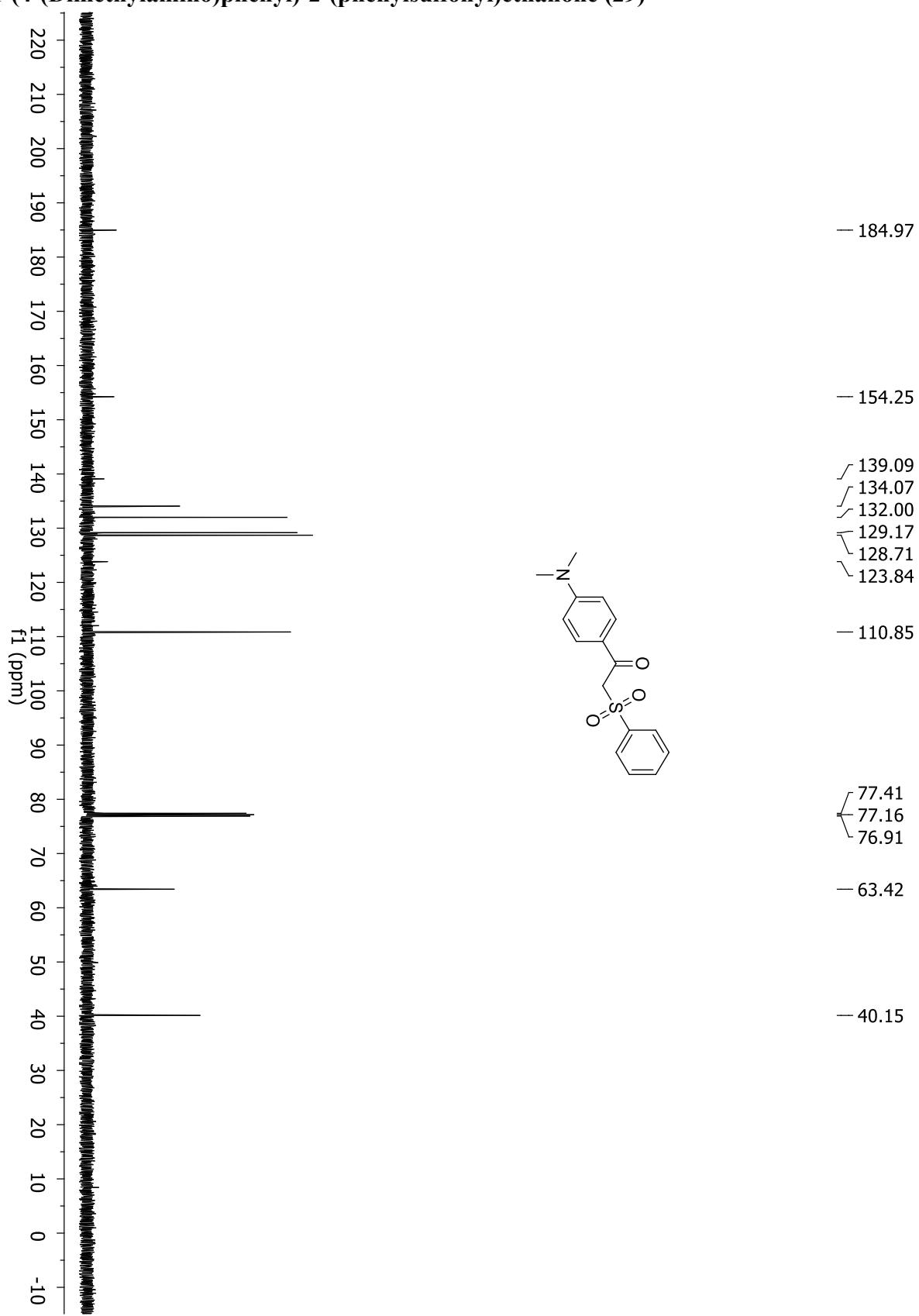
**1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethanone (28)**



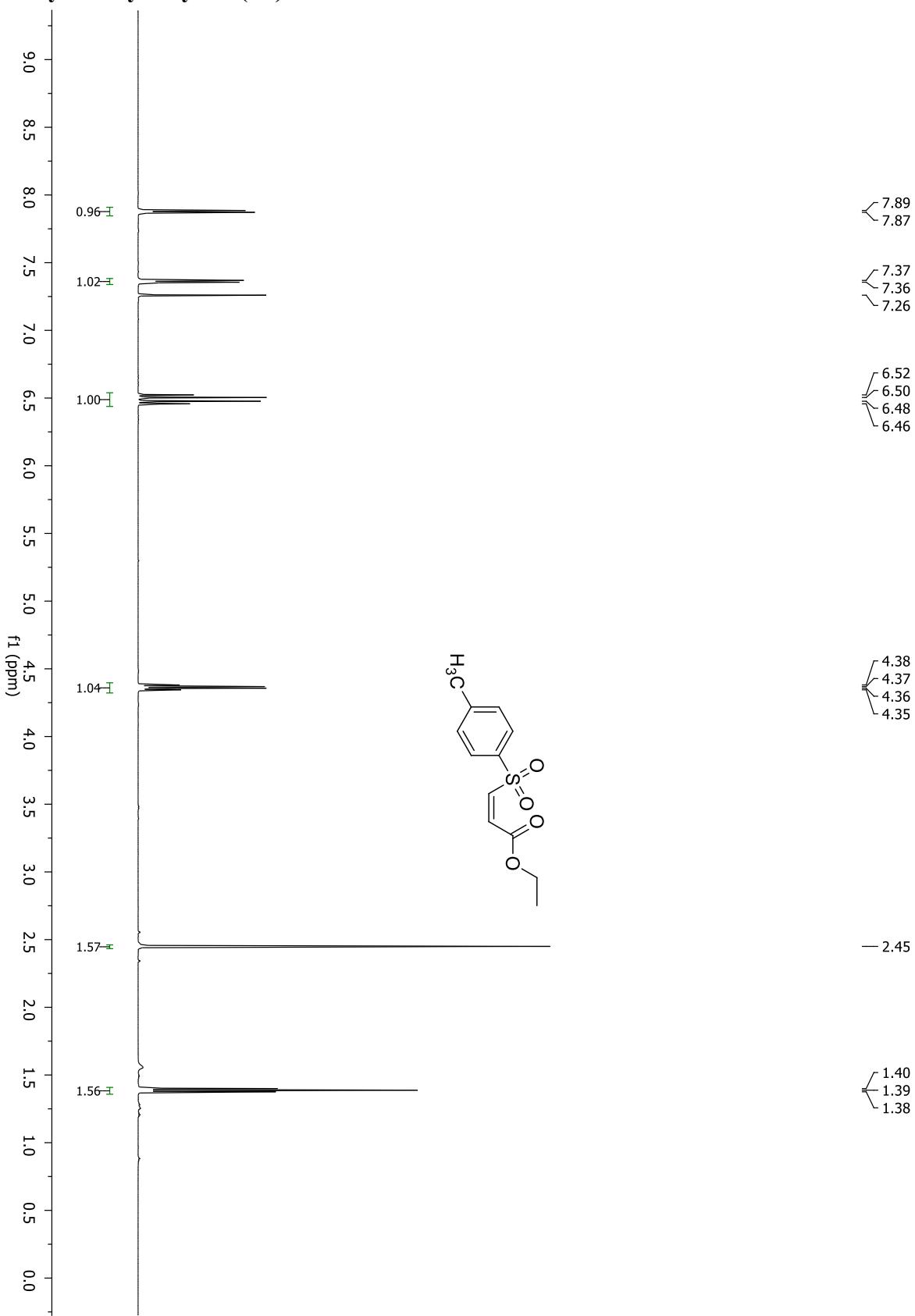
**1-(4-(Dimethylamino)phenyl)-2-(phenylsulfonyl)ethanone (29)**



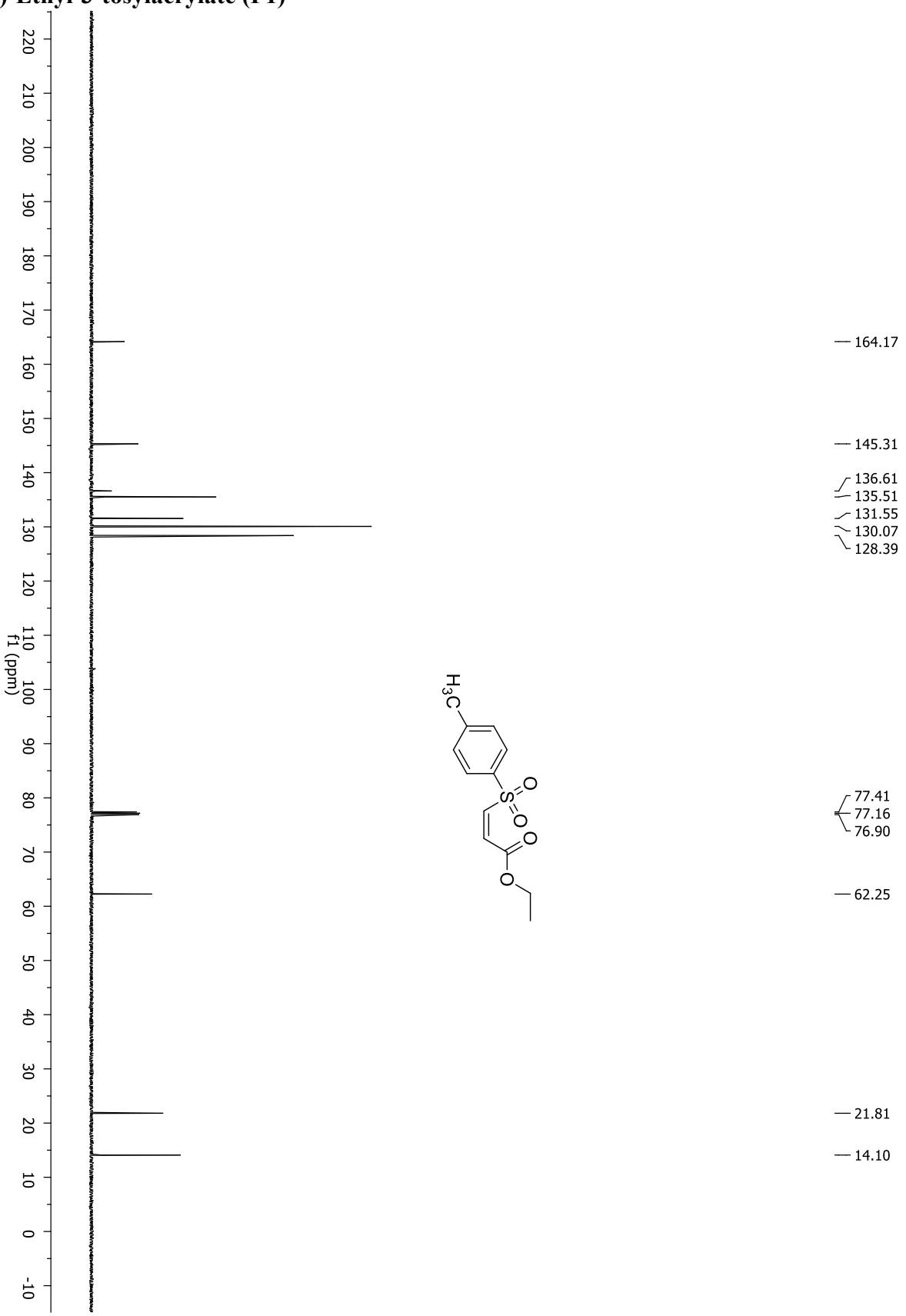
**1-(4-(Dimethylamino)phenyl)-2-(phenylsulfonyl)ethanone (29)**



**(Z)-Ethyl-3-tosylacrylate (P1)**



**(Z)-Ethyl-3-tosylacrylate (P1)**



**(E)-Ethyl-3-tosylacrylate (P2)**

